

UNDER THE MICROSCOPE

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ILLUSTRATIONS BY DALBERT B. VILARINO

New discoveries in energy production, agricultural productivity and chemical catalysis could help clean and protect our planet

BY PIPPA WYSONG

"There must be a better way to make the things we want, a way that doesn't spoil the sky, or the rain or the land." —Paul McCartney

magine a world where crops can clean extra carbon dioxide out of the air and help reduce global warming. Where modified solar panels produce energy that can either be used now or stored for later. And where industry uses novel catalysts that make chemical processes far cleaner than ever before. These seemingly unrelated ideas have one thing in common: they could all contribute to creating a more environmentally sustainable world. They are also getting closer to becoming reality, thanks to research projects supported by the Azrieli Fellows Program.

TWO ENERGY SOURCES IN ONE

When it comes to energy production, the ideal is to have a source that is renewable, clean and always available. But a problem with many renewables is that they generate energy intermittently. Consider solar energy: solar panels collect sunlight and produce electricity while the sun is out, but not at nighttime. Shorter days during the winter months mean fewer hours for producing energy. This means other sources of energy are needed to complement what solar panels can produce, and to maintain a steady flow of energy going into the power grid. But what if you could alter the cells comprising solar panels so that they can do two things: produce energy while the sun is out, and also store it in the form of a clean fuel that can be used later?

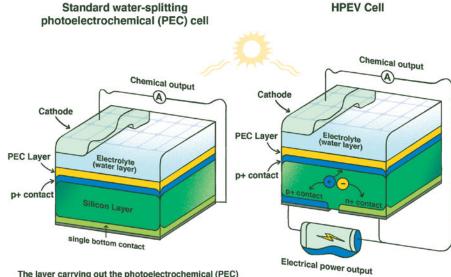
This is exactly what Gideon Segev has achieved with the development of a hybrid solar cell that creates electricity from sunlight while also producing hydrogen gas that can be stored and used later to generate clean energy. This device, a hybrid photoelectrochemical and voltaic (HPEV) cell, is a new concept for solar energy generation and storage. Segev is working on the project as an Azrieli Early Career Faculty Fellow in the School of Electrical Engineering at Tel Aviv University.

It all started in 2007, when he was an undergraduate student in electrical engineering at Ben-Gurion University of the Negev. He read a magazine article about Shai Agassi, former electric vehicle entrepreneur, and the infrastructure of battery-charging stations for electric cars.

"I already had a personal interest in sustainability, and this got me thinking more seriously about working on clean energy, specifically solar energy conversion. That's pretty much the path I've taken since," Segev says.

He spent a year at the Technion – Israel Institute of Technology conducting postdoctoral research in Avner Rothschild's Electrochemical Materials & Devices laboratory. There, he focused on producing hydrogen via solar water splitting: using sunlight to provide the energy for splitting water into its component parts, hydrogen and oxygen.

"A lot of people had looked at developing photoelectrodes [solar cells] that can be put in water, where they will still absorb light and generate current and voltage, but also behave as an electrochemical cell that produces hydrogen by water splitting," he says. But previous designs had components that hindered the performance of the entire device. "We were looking for ways



The layer carrying out the photoelectrochemical (PEC) reaction is usually the performance bottleneck.

The charge that does not contribute to the chemical reaction is extracted by the bottom contacts and contributes to electricity generation.

Adding a second contact to the back (bottom) of the HPEV solar cell enables the collection of electrical energy in addition to the clean chemical energy typically produced by solar cells.

for all of the components to operate at their optimal conditions."

Segev persisted, and in 2016 he joined the Joint Center for Artificial Photosynthesis at the University of California's Lawrence Berkeley National Laboratory to do postdoctoral work under the supervision of Ian Sharp, whose research group deals with experimental semiconductor physics. While Segev was there, the team came up with an improved, workingmodel HPEV cell that successfully extracted more energy from solar storage devices. The breakthrough led to a co-authored publication describing the new model: "Hybrid photoelectrochemical and photovoltaic cells for simultaneous production of chemical fuels and electrical power" (Nature Materials, October 2018).

A standard solar water-splitting device has several layers, each made of different materials and connected in series. The device's performance is determined by the worst-performing layer. Segev bypassed this limitation by adding a contact to the back of the cell, which collected and stored the energy not consumed by the water-splitting chemical reaction.

The HPEV cell prototype is a one-centimetre by one-centimetre square solar cell facing upwards with a thin layer of water on top. The water layer is thin so that full-spectrum light can go through it to the cell. While the cell "Can we also disinfect water while generating electricity and hydrogen?" (functioning as an anode) is operational, the odd oxygen bubble rises from its surface. On the side of the cell is a platinum wire (which functions as a cathode) where hydrogen bubbles form. The hydrogen and oxygen can both be captured and stored. The prototype demonstrated for the first time that an altered solar cell can produce electrical energy while simultaneously producing useful, clean chemicals. The next step is to determine if any water left over from the process could be disinfected by the ultraviolet light hitting the surface of the HPEV cells.

"This is now a major part of my work as an Azrieli Fellow: can we also disinfect water while generating electricity and hydrogen?" Segev says.

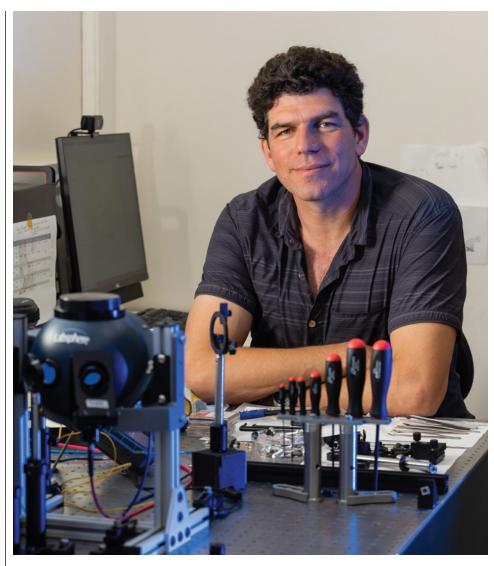
He is currently working with other researchers at Tel Aviv University to investigate more ways to use HPEV cells. In the meantime, there is work to do and refinements to make. The layers of the HPEV solar cells each consist of different composite materials with different energy-absorbing properties. Improving some of the layers could make the hybrid system work better. "In order to advance solar cells further, we will need new materials to go on top of what we currently have," Segev says.

To assess new materials, he and his team use a technique called "spatial collection efficiency extraction," which creates a map of the layers in any kind of photoelectrode to show how well the materials absorb light energy and how much charge they give off. The information indicates where inefficiencies might be.

Segev's journey over the past few years has taken him beyond just electrical engineering in that he's had to learn about material science, chemical engineering and now cleaning water. "It's very interdisciplinary," he says. "You get to learn new stuff all the time. It's a lot of fun."

OPTIMIZING PLANT POWER

Crop yield, agricultural productivity and land use are all intertwined. A rapidly growing global human population (predicted to reach 11 billion by 2100) and intensifying climate change create ever-increasing pressures on land use. This has motivated scientists to look more closely at crop plants. As an Azrieli International Postdoctoral Fellow in bioengineering at the Weizmann Institute of Science, Devin Trudeau made significant strides in helping plants grow more efficiently. This could improve crop yields, which, in turn,



Tel Aviv University researcher Gideon Segev has developed a hybrid solar cell that creates electricity from sunlight while also producing hydrogen gas that can be stored and used later to generate clean energy.

could lead to more efficient use of farmland, for both food and biofuel products.

Trudeau describes himself as a "fullstack bioengineer," borrowing the computer programming term for someone who has the skills to work on an entire system. "I start from the very bottom level, the DNA level, and I try to engineer things all the way up to the organismal level," he says. His interest in biological systems encompasses everything from their basic components—such as proteins—to the metabolic pathways that plants use to convert solar energy to food. His work taps into his knowledge of proteins, genetic engineering and metabolic engineering. He began his investigations into these subjects as a graduate student at the California Institute of Technology, where he helped develop better enzymes for biofuels in the laboratory of Frances Arnold, who later won the Nobel Prize for her work in protein engineering.

"We were trying to design enhanced enzymes to produce next-generation biofuels. We wanted something that worked more efficiently than the enzymes that occur in nature," Trudeau says.

After Caltech, he moved on to the Department of Biomolecular Sciences at the Weizmann Institute. Originally from Canada, Trudeau says he was attracted to Israel first for its warmer weather, but he is also enamoured with the country's strong learning-oriented



"We put the five enzymes together, and showed that this pathway actually worked. It was a new-to-nature metabolic pathway."

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Devin Trudeau co-developed a new-to-nature plant metabolic pathway that could improve improve crop yields, leading to more efficient use of farmland for both food and biofuel products.

culture. As a member of Dan S. Tawfik's group, which focuses on the structure, mechanism and evolution of enzymes, he studied carbon fixation—the process by which plants assimilate carbon from atmospheric carbon dioxide and use it to create simple sugars.

The question was whether a plant's ability to assimilate carbon could be improved. Were there different metabolic pathways that nature hadn't explored? Trudeau explains that there is a certain amount of contingency in evolution: if something works, an evolving organism continues on that path without trying other approaches—potentially missing more efficient paths. The project, FutureAgriculture, was done in collaboration with the late Arren Bar-Even's laboratory at the Max Planck Institute of Molecular Plant Physiology in Germany, and funded by a US\$5.85-million Horizon 2020 grant from the European Commission.

Importantly, the researchers wanted their modified crop plants to use the same amount of light energy, fertilizer and other resources as they did before, yet grow faster and produce more. To achieve this, they addressed a potential inefficiency in carbon fixation known as "photorespiration." This is a net-carbonnegative step that consumes biological energy (in the form of adenosine triphosphate) but leads to the release of some fixed carbon as CO₂. If this loss were avoided, plants could grow more efficiently. Accomplishing this meant taking a close look at the metabolic pathways plants already used, and creating models to determine what other pathways or shortcuts could work. But the models showed there was something missing—none of the enzymes needed for a shortcut existed. It was a challenge that excited Trudeau.

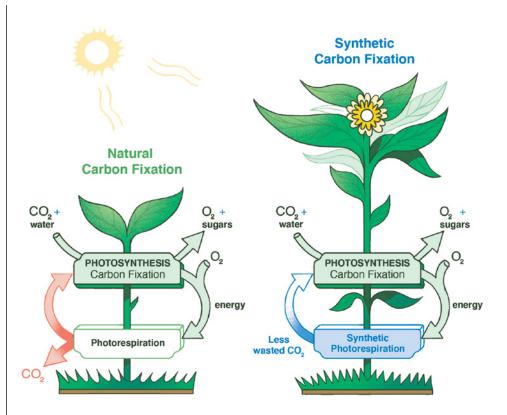
"It was a really interesting question. Can we make this metabolic pathway by evolving new enzymes? Nobody had done this before," he says.

The researchers looked at various possible pathways and picked one that made biological sense and was feasible to engineer. It involved creating two enzymes that didn't exist in nature: glycolyl-CoA synthetase and glycolyl-CoA reductase. Trudeau engineered them from existing natural enzymes with related functions, using a combination of structure-guided directed evolution (a process that mimics evolution to create proteins with new properties) and computational design. To activate the new pathway, the two new enzymes needed to work in conjunction with three other naturally existing enzymes. "We put the five enzymes together and showed that this pathway actually worked. It was a new-to-nature metabolic pathway," Trudeau says. The pathway functions as a module, which means, in theory, it could be used in any plant.

Evogene, a computational biology company in Israel, is now implementing the technique to determine its viability and safety in two types of plants, *Arabidopsis thaliana* (a model for dicot crops like soybeans, tomatoes, potatoes and lentils) and *Brachypodium distachyon* (a model for monocot crops such as rice, corn and beets). In addition to food crops, Trudeau says, the bioengineering technique could be applied to crops used for biofuels, which could replace some fossil fuel products.

Trudeau holds two patents related to his earlier work in biofuels. The first is for an engineered enzyme that degrades cellulose. Processing plants into biofuels requires breaking down their cellulose into simpler sugars. But cellulose is tough, and natural enzymes aren't active enough to break it down sufficiently for the biofuel process. Trudeau's enzyme, a cellulase, is significantly more stable and active at high temperatures. The second patent is for an engineered system of cellulases that work together.

Trudeau is now head of protein engineering at Israeli startup company TargetGene



Biotechnologies, where he works on geneediting systems for potential genetic treatments for human diseases. He uses protein engineering methods to develop novel genomic editing approaches that could complement the CRISPR-Cas9 gene-editing technology.

A new bioengineered pathway allows plants to conserve CO_2 , and thus grow more efficiently and productively than their natural counterparts under the same circumstances.

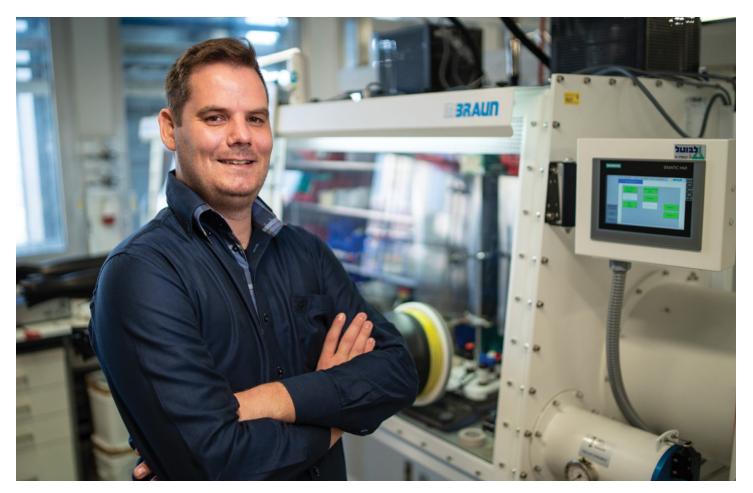
A more eco-friendly food supply could rely on E. coli

Could the proteins we usually get from meat and dairy be produced by bacteria instead? Could the same bacteria be altered to help extract carbon dioxide from the air? While this sounds like something out of science fiction, these are the very questions being investigated by Elad Noor, a computational analyst and metabolic engineer. Noor is an alumnus of the Azrieli Fellowship Program, and he conducted his research at the Weizmann Institute of Science.

As the global population continues to grow, new methods are needed to produce foods that keep up with demand while having a low environmental footprint. Using bacteria to produce the proteins and other nutrients in our diets could be one of the answers. Currently, agricultural systems and food production have high environmental costs, including habitat loss, energy use and greenhouse gas emissions—especially from animalbased products. Generally, plant-based foods have a far smaller environmental footprint and lower energy usage than their animal-based counterparts, yet they provide similar nutrients.

This is where Noor comes in. Through his work at the MiloLab@weizmann in the Department of Plant and Environmental Sciences, he developed a computational model to identify ways to manipulate the metabolic pathways in E. coli bacteria. The purpose was to find more efficient ways for E. coli to conduct carbon fixation, or extract carbon for fuel. Instead of using sucrose or glucose as a carbon source, it could use carbon dioxide from the atmosphere. This may open the door to genetically engineering E. coli and other types of bacteria to use new pathways that facilitate more eco-friendly food production. Details of the work Noor conducted with eight other researchers can be found in "Awakening a latent carbon fixation cycle in Escherichia coli" (Nature Communications, November 2020).

Says Noor: "Bacteria that do more efficient carbon fixing as well as producing proteins could contribute to our food supply while helping us clean the atmosphere." —PIPPA WYSONG



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At the Laboratory for Inorganic & Materials Chemistry at the Technion – Israel Institute of Technology, Graham de Ruiter is researching sustainable organic transformations involving earth-abundant metals.

CLEANER CATALYSTS

Another approach that can contribute to a more sustainable future is to use cleaner substances to trigger chemical reactions for producing materials and chemicals. It is estimated that up to 90 per cent of all chemical processes, whether biological or industrial, require a catalyst. Finding new ones could save enormous amounts of energy and facilitate new chemical reactions that convert unsustainable waste streams into renewable resources.

"This is needed because humanity is at a critical juncture. The amount of human-made mass now exceeds all the available biomass on the planet. Most of this leads to emissions and pollutants that damage the environment," says Graham de Ruiter, head of the Laboratory for Inorganic & Materials Chemistry at the Technion – Israel Institute of Technology. The Azrieli Early Career Faculty Fellow in chemistry is a native of the Netherlands who was drawn to living and working in Israel because of the warmth of the people and "the way they value research and harness intellectual advancement."

In the lab, de Ruiter and his team are developing new catalysts that enable chemical reactivity in cleaner and more sustainable ways. Catalysts are substances that trigger and speed up chemical reactions. They are commonly used throughout industry; however, the processes are often toxic and overall unsustainable.

"It may not be the first thing on people's minds, but where clean energy really starts is with catalysis," de Ruiter says. "It all starts with a tiny molecule that is able to convert one molecule to another. And if you are able to control this, you have the future."

Currently, metals belonging to the platinum group, especially palladium, rhodium and iridium, are widely used as catalysts because they are stable and lead to reactions that are predictable and safe. They are used to produce "It may not be the first thing on people's minds, but where clean energy really starts is with catalysis." materials ranging from plastics and fertilizers to pharmaceuticals and specialty chemicals.

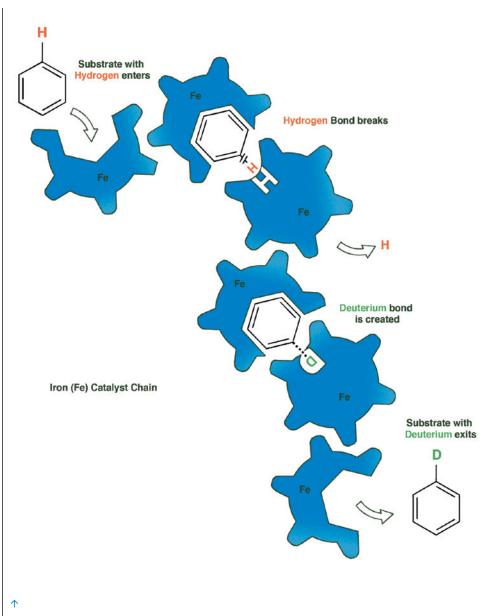
A commonly used reaction that involves a catalyst is the formation of carbon-carbon bonds, which are needed for a wide range of applications. Nature regularly makes carbon-carbon bonds using highly specialized enzymes (nature's catalysts) that contain common metals, such as iron. In fact, the past decade has seen a surge of interest among chemical scientists in mimicking these processes.

These carbon-carbon bonds introduce—as chemists call it—chemical complexity, and they are a key component in developing new pharmaceuticals. An example is the production of eletriptan, a selective serotonin agonist used to treat migraines. Here, a palladium catalyst is used to make the carbon-carbon bonds necessary to create the chemical that forms the drug. However, mining the geological deposits that contain platinum metals generates high carbon footprints and destroys the ecological habitats in which they are found.

To find substitutes, de Ruiter and his team are investigating earth-abundant metals such as iron, manganese and cobalt. All three are common and cheap, and they have lower environmental footprints than the platinum metals. But one cannot simply replace palladium with iron. For one thing, these metals differ in their basic reactivity. So far, iron, manganese and cobalt haven't done the job as predictably as platinum metals.

From a chemist's point of view, "iron is like a teenager among the transition metals— it's not mature and does whatever it wants. It is always difficult to control," de Ruiter says, adding that to overcome this limitation, "we're using nature and the way enzymes work as inspiration. We're trying to take the design principles that we find in nature and apply them to chemical transformations that are of interest to industry and academia."

One aspect of de Ruiter's work is manipulating the chemical environment surrounding the metal ions, or ligands. Altering the electronic properties of the ion's metal centre makes its chemical reactivity more predictable and reliable. In fact, his lab developed a new ligand system that successfully controls the reactivity of iron. The system can selectively replace hydrogen atoms with deuterium atoms in a hydrogen-deuterium exchange process. Deuterium, or hydrogen-2, is an isotope of hydrogen that is widely used as a



Using iron catalysts in chemical reactions provides a less toxic and more efficient pathway for isomerization (rearranging molecules' structures to create industrially useful compounds).

non-radioactive tracer in the pharmaceutical industry, and de Ruiter's system provides a cleaner way of producing it.

The team also developed an iron-based catalyst for the isomerization of alkenes—a process important in the chemical industry. Alkenes are hydrocarbons with double carbon-carbon bonds. Isomerization is a process in which part of a molecule is rearranged. The new catalyst lasts longer and works more efficiently than those using the platinum group metals.

"Some of the most active catalysts that do this are based on iridium. Each iridium catalyst can be used 19,000 times. But this new iron catalyst can be used 160,000 times, with the same general benefits seen from iridium," de Ruiter says. The implications are that the amount of iron needed for chemical reactions is much lower, plus it lacks iridium's toxicity. The findings will be published in a paper later this year.

Catalysts are used in such a wide range of industries that replacing standard platinum-metal catalysts with ones made from earth-abundant metals could go a long way towards conserving the environment and reducing carbon emissions.

Says de Ruiter: "This is really the pinnacle of sustainability." •