

PHOTO: FRITZ HABER INSTITUTE OF THE MPS

Multi-purpose research station: the Berlin-based Max Planck team is able to observe experiments within this vacuum apparatus using various instruments. The steel hemisphere on top contains the analyzer for measuring the energy of photoelectrons.

GREENHOUSE GASES ELECTRIFIED

TEXT: KARL HÜBNER

In future, the greenhouse gas carbon dioxide could be used to create important chemicals and fuels. If this vision becomes reality, it would be a major step towards achieving a sustainable circular economy. The Interface Science Department of Beatriz Roldán Cuenya at the Fritz Haber Institute of the Max Planck Society in Berlin is working toward this very goal.

The concentration of CO₂ in the atmosphere is inexorably rising – which has well-understood consequences for the climate. Stopping this process is a task of mammoth proportions. Yet in some areas, such as waste incineration or cement production, it is almost impossible to avoid producing carbon dioxide exhaust. One option is capturing the gas at the point where it is released and disposing of it in underground storage facilities. Another possibility is to use it as raw material for synthesizing fuels and chemicals as a way of carbon recycling. Such CO₂-neutral production would have two positive impacts: avoiding direct CO₂ emission and reducing consumption of fossil raw materials.

Research groups around the world, including some at the Max Planck Society, are working on ways to utilize carbon dioxide as a raw material for the production of useful chemicals (see

MaxPlanckResearch 3/2021). Indeed, the gas is already being processed industrially, together with hydrogen, to produce methanol – a raw material of major importance in the chemicals industry. Furthermore, a research group led by Walter Leitner, Director at the Max Planck Institute for Chemical Energy Conversion, is collaborating with a team from Covestro AG to develop another special process. For several years now, a polymer has been partially derived from CO₂ that is used to produce foams used in mattresses (see MaxPlanckResearch 2/2019). The method reduces consumption of the crude oil from which the corresponding polymer component is usually extracted. Nevertheless, using CO₂ in chemical processes is no simple matter, because it is highly stable as a molecule. A substantial amount of energy has to be spent to make the molecule responsive, which is why high pressure and high temperature are required for such methanol synthesis. There is another approach, however: using electrical instead of thermal energy to get CO₂ to react. This represents an electrocatalytic route comparable to the electrolytic generation of hydrogen from

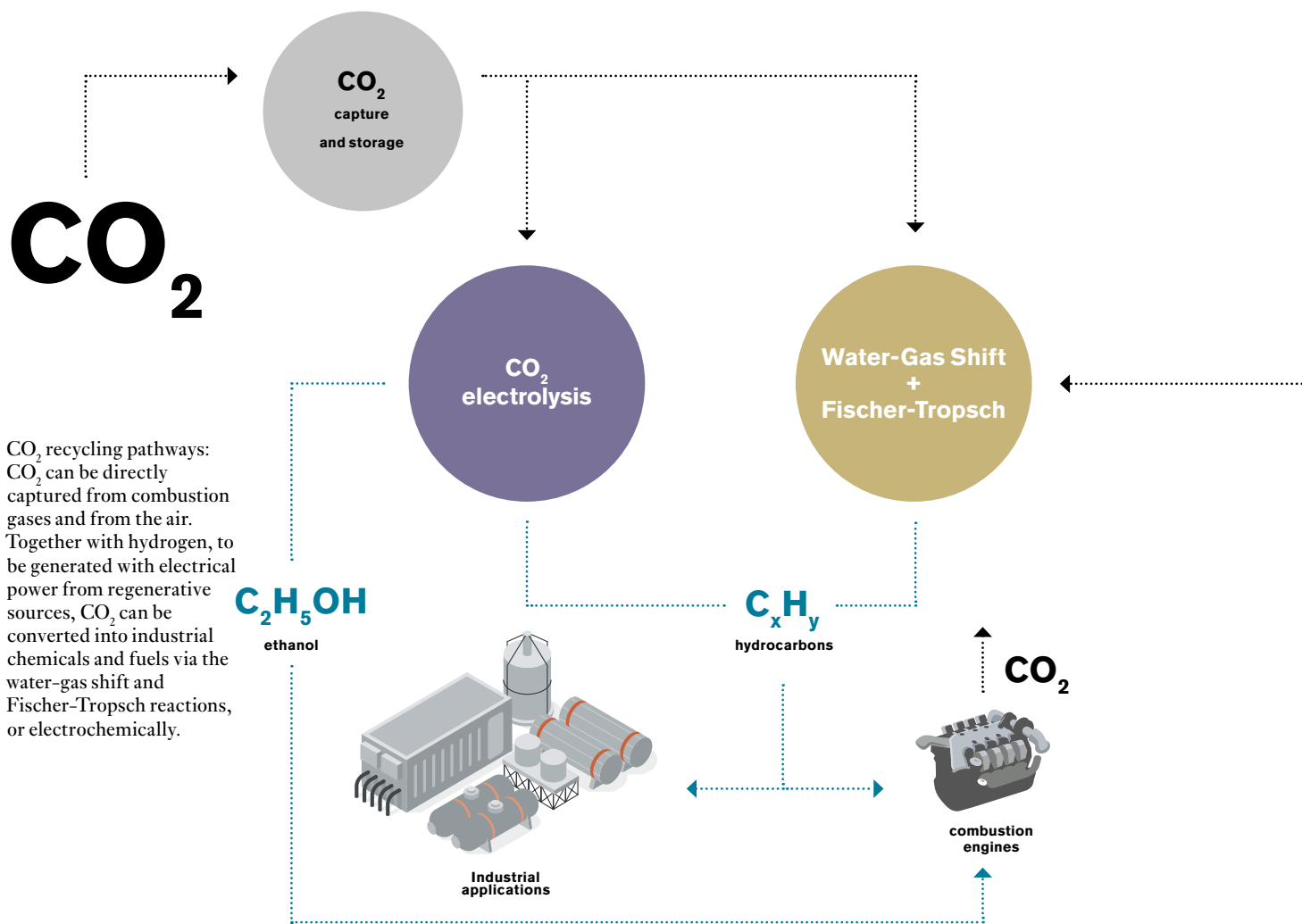
water. Ideally, of course, the electricity required for the process should be “green” – for example, derived from solar or wind power.

Carbon monoxide (CO) is a possible by-product of CO₂ electrolysis. It is possible to obtain numerous important basic chemical substances from this gas, in combination with hydrogen (which should also be produced using renewable energies). What’s more, the necessary industrial infrastructure for this already exists. A further idea is the direct electrocatalytic production of some of these basic chemicals from CO₂ (and water). This avenue is being explored by a team led by Beatriz Roldán Cuenya, who is Director of the Interface Science Department at the Fritz Haber Institute in Berlin, part of the Max Planck Society.

The researchers are especially interested in ethylene (also known as ethene) and ethanol. “Those substances are of great interest due to their high energy content, and because they are easy to store,” explains Beatriz Roldán Cuenya. Furthermore, ethylene is the base substance for plastic polyethylene (PE), the most important plastic

55





CO₂ recycling pathways: CO₂ can be directly captured from combustion gases and from the air. Together with hydrogen, to be generated with electrical power from regenerative sources, CO₂ can be converted into industrial chemicals and fuels via the water-gas shift and Fischer-Tropsch reactions, or electrochemically.

SUMMARY

Numerous research groups around the world are working on obtaining fuels or substances for chemical production from carbon dioxide.

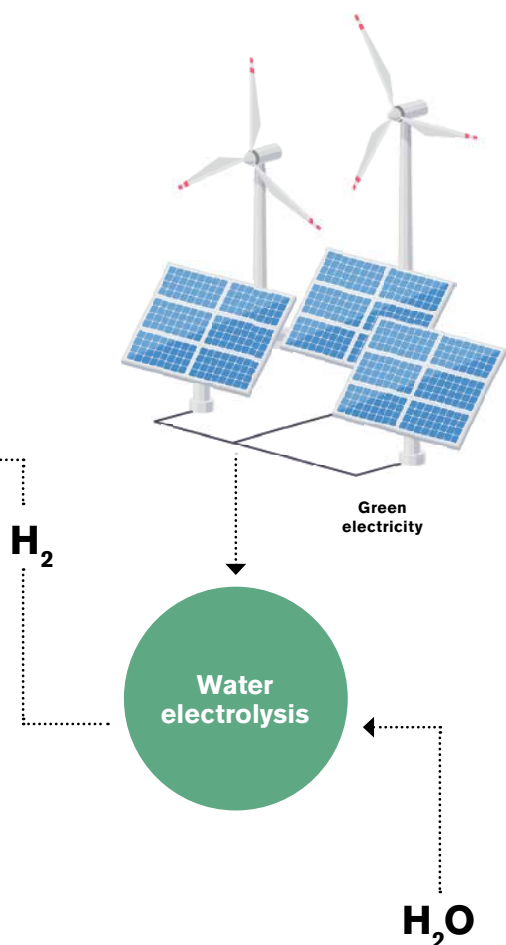
The team led by Beatriz Roldán Cuenya is trying to use electrolysis for the targeted production of fuels and industrial chemicals through high-yield processes.

Experiments have shown that the size, shape and chemical properties of the copper catalyst required make it possible to influence the reaction, so as to promote the creation of either ethylene or ethanol.

quantitatively speaking, and a key building block in many chemicals used in widely different industries. In the past, ethylene was produced exclusively from fossil raw materials. Ethanol, on the other hand, is suitable for use as a fuel due to its good combustibility, and it is already being added to premium petrol. For Roldán Cuenya, ethanol and ethylene are and will be “essential molecular building blocks of chemistry,” even in the longer term. The physicist thus believes that fossil-free production of these substances from CO₂ and green hydrogen is a “high-priority goal in chemical energy conversion efforts.”

From a scientific perspective, one of the primary tasks is to develop suitable catalysts for the production of ethylene and ethanol. This is what the Berlin-based researchers are doing

for the electrolysis of CO₂ but also for the electrolysis of water, which is split into hydrogen and oxygen in the process. Roldán Cuenya’s team is currently working on catalysts for splitting water molecules that can replace the costly use of iridium, which is commonly used for the oxygen evolution reaction. The objective: to make the entire electrolysis process, and hence hydrogen synthesis, more economical. Great hopes are pinned on green hydrogen as a possible replacement for fossil raw materials one day, for example, in the steel and chemical industries. Green ammonia could also be synthesized this way, thus functioning as a storage medium for (green) hydrogen, facilitating its transport in tankers and through pipelines. Additionally, ammonia is the primary raw material used in the production of artificial fertilizers.



Returning to CO₂ electrolysis, the good news is that it is already possible to obtain the two desired substances ethylene and ethanol from CO₂ through electrolysis. Clara Rettenmaier, a PhD student in Roldán Cuenya's department, showed us what this looks like on a small scale in a lab at the Fritz Haber Institute. She presented a cylindrical glass vessel containing a colorless liquid with gas bubbling through it. Inserted into the liquid is a kind of stylus, with a one cent coin attached to the bottom. "The stylus serves as the electrode; we apply voltage to it to reduce the CO₂ released into the water through the gas bubbles. The copper coin is our catalyst," explains the chemist. The coin makes the demonstration more striking for visitors. The actual catalysts used are much smaller – copper nanoparticles invisible to the human eye.

With a few clicks on a computer just next to the lab apparatus, the chemist calls up measurement curves that provide information about the products formed. "That's the ethylene there," says Clara Rettenmaier, pointing to a peak in a curve. Moving her finger on to further spikes, she continues: "And that's methane, this is carbon monoxide, and up here we have hydrogen."

In search of a process selection mechanism

The problem the research group is intensively working on can be described as a search for a process selection mechanism. "Theoretically, a whole range of compounds can be created from CO₂, but unfortunately, they often form at the same time," explains Roldán Cuenya. Another problem is that the applied voltage simultaneously also splits water into hydrogen and oxygen. Since product mixtures make further processing complicated and expensive, it is important to have an economically feasible process in which the single desired substance is obtained with maximum yield, as Roldán Cuenya further elaborates.

Thus, the question her research department is addressing is: how can elec-

trolysis be controlled so as to maximize production of ethylene, or ethanol? Clearly, the right catalyst is required for this. The basic job of the catalyst is to break the bonds of CO₂ and stabilize certain intermediate products to enable new bonds to form. Roldán Cuenya's team is studying precisely what happens on the surface of the catalyst during the reaction process, namely, how the material reacts and adapts to the reaction conditions.

To date, copper has been the only known catalyst material that can electrochemically convert CO₂ into compounds with two or more carbon atoms. The necessary carbon-carbon coupling process in electrolysis occurs only with copper. This is apparently the case because the distances between the copper atoms in the copper metal lattice and the strength of the bonds between the copper and carbon atoms are optimal.

Unlike in the apparatus used for their demonstration, the actual experiments do not involve a copper coin but rather tiny little copper oxide cubes. The Berlin-based team produces these so-called "nanocubes" themselves – you would have to line up about a thousand of the cubes to equal the diameter of a hair. The tiny cube shape means the copper has a

57

Depth at surface level: Lara Celeste Chaves, Rosa Maria Arán-Ais, Clara Rettenmaier, Antonia Herzog, and Beatriz Roldán Cuenya (from left) study ways of controlling the electrocatalytic conversion of CO₂.

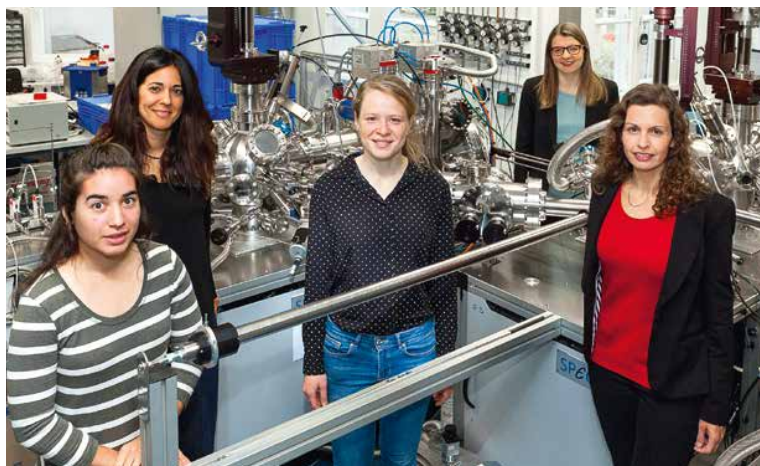
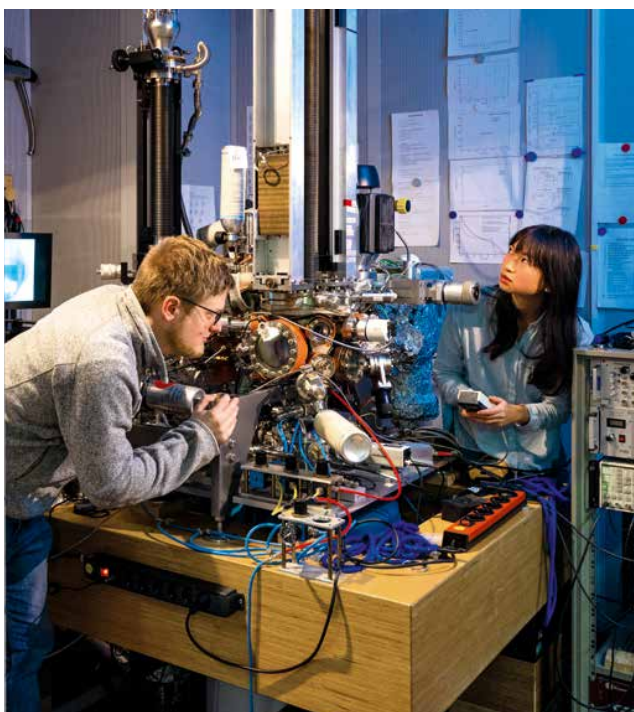


PHOTO: FHI / CHRISTIAN TESSMAR

Nanosopic surface exploration: Felix Landwehr and Claudia Khanh-Ly Nguyen adjust an atomic force microscope usable to create profiles of surfaces.



58

much larger surface area per gram than a cent coin, so with the same amount of copper, much more CO₂ can react. The researchers affix the catalyst cubes directly to the electrode, which is then immersed in CO₂-saturated water. In addition, the water's electrolytic properties have been improved using dissolved potassium salt.

The electrolytic cell will fit into a coffee cup, but the Berlin research group employs entire rooms full of equipment. This is because with some measurement methods, the smaller the structure that is to be studied, the more space is required. Ultimately, the researchers are interested in what happens to the catalyst at the atomic level during electrolysis, which means on the scale of a millionth of a millimeter. The department maintains a vast range of equipment to render this visible in complete chemical and physical detail, distributed over several large laboratories in multiple buildings. Roldán Cuenya and her team have modified certain methods, such as electron microscopy, to allow their use in the aqueous environment of electrolysis.

In some cases, multiple measurement technologies have to be combined for a single experiment. Doing so was necessary, for example, to reveal that the actual active centers of the catalyst material only form under reaction conditions, and that these constantly change during the process. Using liquid-phase electron microscopy, the team has now also made visible other changes in the catalyst that occur during CO₂ electrolysis. “We have observed that the catalyst cubes change their shape and size during the electrolysis process,” explains Roldán Cuenya. Clearly, such morphological changes affect catalytic properties as well. Routine use of this process in an industrial setting would thus only be possible once it is known how to stabilize the active phases of these catalysts.

Another of the team's key findings is that the active centers of the catalyst for the undesired side reaction – in which hydrogen is split off from water – differ from the active centers for the electrocatalytic reduction of CO₂. Furthermore, the researchers have also discovered that there is apparently an ideal cube size. “If the cubes

are too small, they simply detach and accumulate elsewhere,” says Roldán Cuenya. This is disadvantageous, she notes, because such agglomerations mean a loss of catalytically active surface area.

However, the catalyst also changes chemically in the course of the reaction, as experiments using X-ray photoelectron spectroscopy have shown. The textbook rule that a catalyst does not change in the course of a reaction is thus not true in all cases. The pre-catalyst was initially in oxidized form owing to the production process, but gradually this was reduced until a certain proportion of elemental copper was reached. The problem: this steers the reaction in a different direction than the oxide.

Anti-aging cure for the catalyst

The scientists devised a clever idea for controlling the conversion to pure copper during the reaction: simply reversing the process after a certain period by applying a voltage with opposite polarity. That served to re-oxidize the metallic copper atoms, regenerating the catalyst to some extent. The group commenced experiments in which they applied voltage in pulses, switching between positive and negative polarities. As predicted, the procedure did indeed effectively reverse changes in the catalyst, prompting Roldán Cuenya to call this an “anti-aging” procedure. But regularly switching the voltage between positive and negative had another effect as well: it acted as a selectivity lever, because the duration of the respective pulses can be used to promote the formation of certain products. Long reduction pulses, for example, promote the production of ethylene, while long oxidation pulses produce more carbon monoxide. Furthermore, long reduction pulses of several seconds' duration combined with short oxidation pulses significantly increases ethanol yield.

The extensive analysis conducted by the team has now enabled good visual

rendering of precisely what happens. For example, the researchers observed that more ethanol is synthesized when thin, disordered copper oxide clusters form on the surface of elemental copper. Ethylene, in contrast, appears more likely to form on elemental copper than on oxidized copper. This provides a plausible explanation for why longer reduction pulses promote ethylene synthesis. The methods employed by the team at the Fritz Haber Institute in Berlin are also effective, among other things, for identifying the influence on electrolysis of defects or foreign metal atoms in the lattice of copper atoms. Thus, it emerged that ethanol synthesis is accelerated by adding five-percent silver.

A contribution to fighting climate change

These are all just initial insights into possible ways to achieve selectivity. “The main thing right now is to gain a better understanding of the mecha-

nisms,” emphasizes Roldán Cuenya, adding: “You just can’t make a leap before you’ve learned how to walk.” In other words, we still have a lot to learn before it will be possible to custom-design the optimal catalyst for a specific desired reaction and bring it into large-scale industrial usage.

Industrial applications may still be a long way off, but for the Max Planck Director Roldán Cuenya, conducting “fundamental research with social relevance” is important. She envisions that sometime in the future, electrochemical processes will be conducted with CO₂ right out of the air. Research is already underway at various institutions into the direct air capture technologies required for this. Roldán Cuenya believes that achieving a complete restructuring of the energy and chemicals industries around sustainability objectives will pose one of the greatest challenges society faces in the fight against climate change. And she hopes to contribute to these efforts with her work.

GLOSSARY

ELECTROLYSIS

An electric current between two electrodes in an electrolyte is used to chemically transform substances. One electrode (the anode) takes on electrons from a substance within the electrolyte, while the other (the cathode) gives up electrons to another substance.

LIQUID PHASE ELECTRON MICROSCOPY

Electron microscopy is a high-vacuum microscope that uses an electron beam to depict atomic structures. Beatriz Roldán Cuenya has found a method enabling the study of samples in liquids that under normal conditions would immediately evaporate.

CATALYST

A substance that lowers the energetic hurdle for a reaction to occur, thereby enabling or facilitating the formation of certain products.

X-RAY PHOTOELECTRON SPECTROSCOPY

A technique in which an X-ray beam releases electrons from the surface of a sample; these electrons provide information about the chemical properties of the surface.

Controlled reaction: carbon monoxide and methane (left cube) are the primary products generated during electrolytic reduction of CO₂ on nanocubes with substantial copper oxide on their surface. The reaction proceeds in this direction if the polarity of the reducing voltage is regularly reversed over an extended period of time (left square graph), so that the surface is oxidized. Less oxide forms on the surface if the oxidation pulses are shorter, in which case ethanol is the main product (center cube). Long reduction pulses keep the surface free of oxides, resulting in CO₂ being reduced to ethylene (right cube).

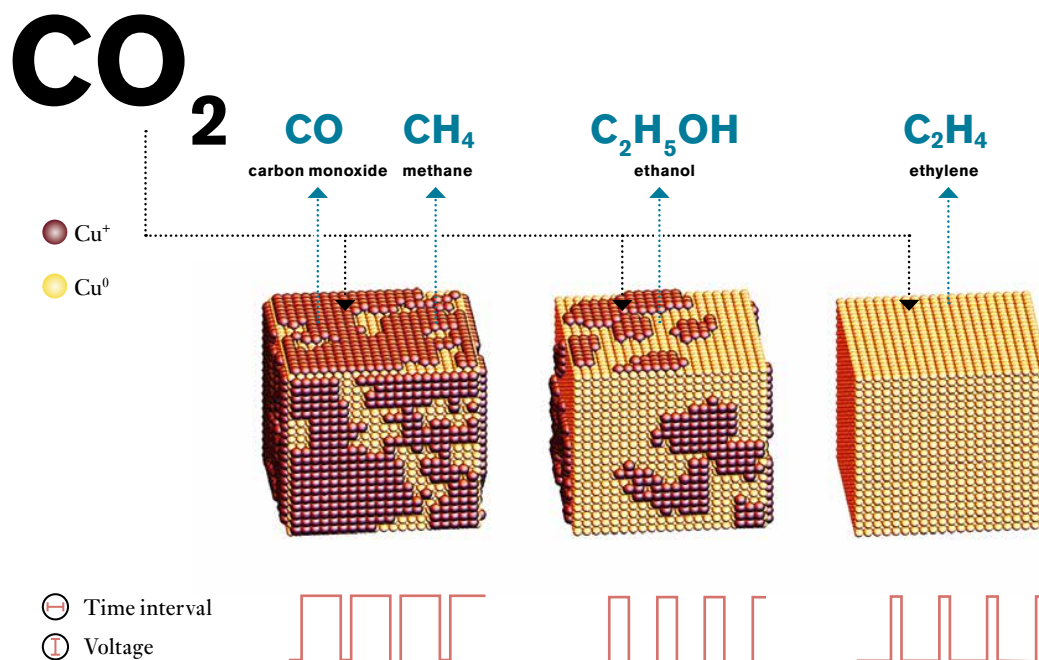


CHART: GCO ACCORDING TO TIMOSHENKO, J., BERGMANN, A., RETTENMAIER, C., ET AL. STEERING THE STRUCTURE AND SELECTIVITY OF CO₂ ELECTROREDUCTION CATALYSTS BY POTENTIAL PULSES. NAT CATAL 5, 259–267 (2022)