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This feature explores how Associate Professor Takashi Yamamoto is using "electro-organic synthesis" to find green and sustainable ways for manufacturing processes.

Electrifying Organic Synthesis

Synthesizing organic compounds using electricity, known as "electro-organic synthesis," has received a world-wide attention for its potential in reducing CO_2 emissions and reagent wastes, thereby realizing a more sustainable manufacturing process. In this increasingly competitive field, Associate Professor Yamamoto hopes to replace conventional manufacturing with new methods through his own unique approach.

Organic compounds essential for our daily life

We are surrounded by man-made objects. Among them, organic compounds (carbon-based substances) play a vital role in our daily life, as plastics, elastics, synthetic fibres, and pharmaceuticals.

Synthesis of organic compounds generically requires "special reagents", e.g. catalysts, to accelerate chemical reactions. In addition, huge amounts of energy are often required because some reactions take place at high temperature. Of course, while most reagent wastes produced from the reactions are properly collected and disposed of, the environmental impact could be significantly reduced by excluding such reagent wastes from the process.

This is the background of "electro-organic synthesis". Associate Professor Yamamoto at the Department of Chemistry is one of the leading researchers in this exciting field.

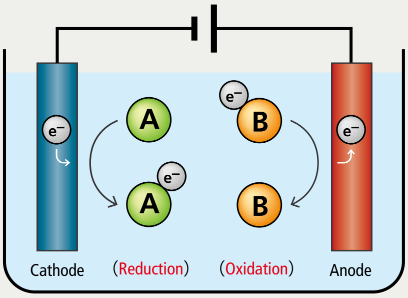
Electro-organic synthesis?

Do you remember learning about electrolysis in junior high school? When an anode and cathode are immersed in water (H_2O) and electricity is applied , hydrogen (H_2) is generated at the cathode and oxygen (O_2) is generated at the anode. "Electro-organic synthesis" applys such electron transfer events to create new organic compounds from other organic compounds (Figure 1). A chemical reaction is driven by electricity instead of special reagents.

Main achievement during a short-term study at the University of Mainz

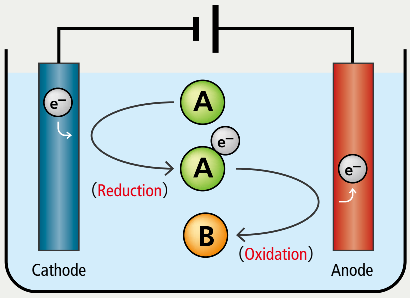
Yamamoto started researching electro-organic synthesis in 2016, when he stayed at Johannes Gutenberg University Mainz (University of Mainz) in Germany. "At that time, I was struggling to keep up with the speed of research field that I had been working in, so I was feeling quite anxious about my future. Fortunately, I was given the opportunity to study abroad through the Keio University Ishii-Ishibashi Fund for Young Researchers. At the time, I had been working as a

(A)



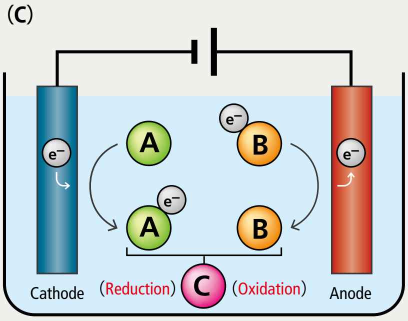
Substance A is reduced at the cathode while substance B is oxidized at the anode. Both substances are desired products.

(B)



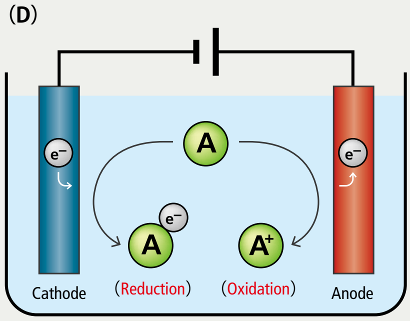
Substance A is first reduced at the cathode, then oxidized at the anode, forming a desired product B.

(C)



Substance A is reduced at the cathode and substance B is oxidized at the anode. They react to form a desired product C.

(D)



Substance A is reduced at the cathode and oxidized at the anode, resulting in desired products.

Fig.1
Paired electrosynthesis for more efficient use of electricity
Reduction (receiving electrons) and oxidation (losing electrons) occurs at the cathode and anode, respectively. Activated species by this process react to produce a desired substance. Even though electro-organic synthesis does not use special reagents, energy is wasted if the electricity is not used efficiently. In order to avoid this problem, researchers in electro-organic synthesis have been developing "paired electrosynthesis," which leads to the synthesis of target substances at both the cathode and the anode.

senior assistant professor with Professor Yasuaki Einaga. I wanted to try breaking new ground that can be continued when I returned to Japan. Since Professor Einaga is working on the chemistry of diamond electrodes, I searched a research topic related to the diamond electrodes." Thus, I began research on electro-organic synthesis using diamond electrodes with Professor Siegfried R. Waldvogel at the University of Mainz.

In 2017, he succeeded in synthesizing α-diisoeugenol from isoeugenol (Figure 2). "Even though the starting material was the same, when solvent was changed and applied an electric current, the products were different from what I expected. Even though I had been studying chemistry for a long time, I was so shocked that such a thing happens."

This is not the only thing to shock Yamamoto. In chemical synthesis, stereoisomers—isomeric molecules that have the same chemical formula, but different spatial arrangements of their atoms—are obtained mixed together without any special trick. Because stereoisomers have different properties, it is necessary to separate them once mixed. Therefore, one of the major challenges in chemical synthesis lies in easily produce only the stereoisomer of interst. To return to Yamamoto's experiment,only α-diisoeugenol was produced and no other stereoisomers were present.

Based on what he learned and achieved in Germany, Yamamoto is now working electro-organic synthesis using diamond electrodes at the Einaga Group.

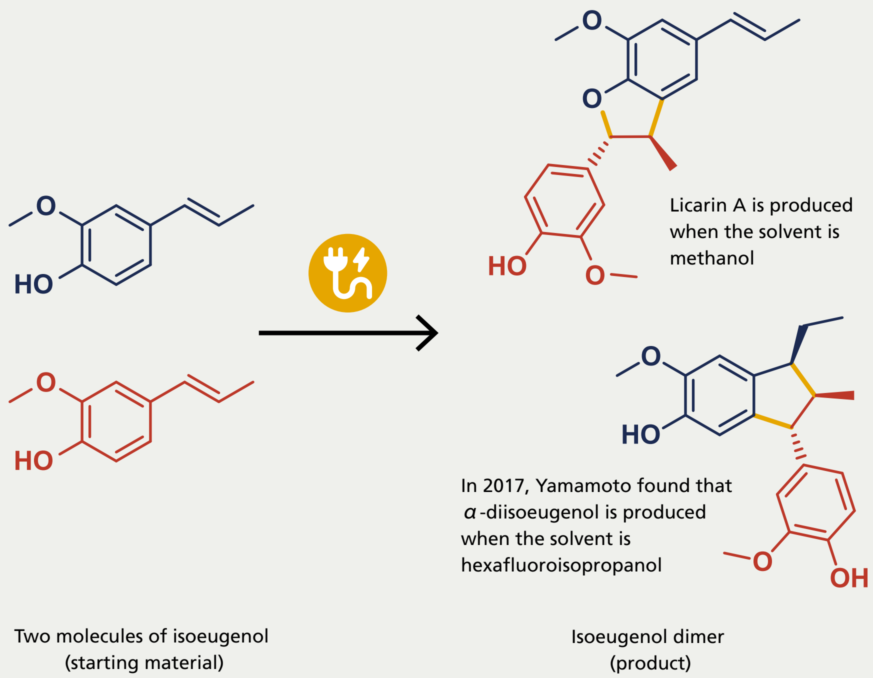


Fig.2

Electro-organic synthesis using isoeugenol as a starting material

This is the main achievement that Yamamoto had done in University of Mainz. When hexafluoroisopropanol was used as a solvent, α-diisoeugenol was formed from two isoeugenol molecules (bottom). Previously, it was known that licarin A was formed when methanol was used as a solvent (top). It was a big surprise that changing the solvent had a strong impact on the product. Yellow lines indicate newly formed bonds.

Intense competition in green and sustainable manufacturing

The situation has changed since Yamamoto has started researchin electro-organic synthesis,. "Attempts to synthesize substances using electricity have a long history, dating back to the 1800s. In the late 1900s, the field of electro-organic synthesis made great progress, but the number of researchers working in this field did not increase significantly because of the lack of equipment that anyone could easily handle. Now, however, the situation is completely different. Various companies sell electrosynthesis equipment that is easy to use, lowering barriers to starting research in electro-organic synthesis. Electro-organic synthesis not only avoids the use of special reagents, but also allows power to be supplied from renewable energy sources such as solar power and wind. Therefore, electro-organic synthesis is undergoing a worldwide development race, as enables manufacturing that can reduce CO_2 emissions."

Competing with the world through research that only I can do

However, Yamamoto is not anxious about the future of his research as he used to be. This is because he is absolutely confident in the electrode material that is a significantly important factor in electro-organic synthesis.

"The diamond electrodes prepared at the Einaga Group have several excellent properties for electro-organic synthesis that other electrodes do not have. I will explain two representatives. First, the highly reactive radical species that are produced by applying electric current are stable at the surface of diamond electrodes. Second, diamond electrodes can be used over a wide range of voltages. Overall, diamond electrodes enable to realize chemical reactions that would not be possible with commonly used electrodes."

Yamamoto is also attempting to make own improvements to their diamond electrodes. "My previous research project was developing the optical and magnetic properties of inorganic nanosheets towards next-generation devices. I can make a modification of the electrode surface based on the experiences and techniques I acquired from those studies. It is really interesting to see how changing the properties of electrode surface influences on a yield and selectivity of products. I aim to pioneer a new 'science of electrodes' by establishing a fundamental theory behind these phenomena."

Yamamoto also talked about the various things he aims to accomplish. His ultimate goal is to "realize chemical reactions in electro-organic chemistry that even high school students can understand." "An example would be to replace the reactions that are already in textbooks and used in industry (e.g. reactions that require high temperatures and pressures) with electro-organic synthesis. Realizing this goal would be the only way I can say that I have achieved green and sustainable manufacturing."

Electro-organic synthesis is currently facing a wave of intense competition. Yamamoto is drawing on his breadth of experiences and making strong strides forward to achieve his impressive goals as a researcher.

(Interview and text writer: Akiko Ikeda)