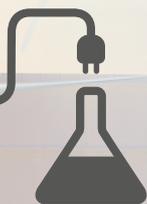


FRAUNHOFER LIGHTHOUSE PROJECT ELECTRICITY AS A RESOURCE

**ELECTRICITY
AS A RESOURCE**





GREEN ENERGY FOR SUSTAINABLE CHEMISTRY

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Fraunhofer Institute for Environmental, Safety, and Energy Technology (UMSICHT).

In 2017, more than one-third of Germany's electricity came from renewable energy sources – a growing trend. The progress of the energy transition is reducing the level of CO₂ used for electricity and opening up new paths for electricity-driven production. Nine Fraunhofer institutes are now pooling their competences in order to develop and optimize new electrochemical processes, under the motto "Electricity as a resource", for manufacturing important basic chemicals.

THE RENAISSANCE OF ELECTROCHEMISTRY

A climate-neutral supply of energy and carbon-intensive raw materials is possible if there is a fundamental transformation of the energy and raw materials system that takes societal and economic needs into account. The new "raw materials" are sustainably provided carbon and renewable, primarily fluctuating energy sources. Electrochemical processes make these raw materials available for the chemical industry and turn them into products with a "green footprint". Electrochemical processes are key technologies for connecting the energy system to chemical production.

Electrochemistry can supplement or replace catalytic thermochemical processes – as long as its use also provides advantages in terms of efficiency or sustainability. Until now, there has hardly been any systematic research on new electricity-based synthetic pathways for using green electricity in the production of basic chemicals. New, integrated process concepts were quite uncommon, as were plant engineering, process materials – such as catalysts – and qualifying analytics.

The Fraunhofer lighthouse project "Electricity as a resource" has now developed the necessary competences, products, processes and services for the process industry and the energy sector. They will be provided under the eSource® brand as a technological research, development and education platform.



THE RESULTS AT A GLANCE

The "Electricity as a resource" lighthouse project has developed new electrochemical processes, demonstrated them at the technical level, and analyzed their connection to the German energy system. The following results have been obtained:

Electrochemical processes

- Producing hydrogen peroxide (H_2O_2)
- Converting carbon dioxide (CO_2) to ethene (C_2H_4)
- Converting carbon dioxide (CO_2) to short-chain alcohols and acids (high-pressure electrolysis)
- Converting carbon dioxide (CO_2) to long-chain alcohols (high-temperature co-electrolysis and optimized Fischer-Tropsch process)

Components

- Optimized catalysts
- New electrode systems
- New ion-conducting polymer membranes

System evaluation

- Modeling and optimization tools
- Market analyses and business models
- New methods for assessing sustainability

Fraunhofer offers the following range of competences for innovations in electrochemical syntheses:

- Process development as well as constructing and operating pilot plants (batch and continuous operation)
- Developing and testing (electro-) catalysts, cells, and stacks
- Procedures for manufacturing and testing electrodes for electrochemical processes
- Developing ion-conducting polymer membranes
- Analyzing and characterizing catalysts, electrodes, cells, and membranes
- Modeling, simulation, and optimization
- System analysis and sustainability assessment
- Innovation management
- Project and business-model development

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H₂O₂ ON DEMAND

1 Stack for electrochemical production of H₂O₂.

2 Electrochemical process development in the lab.

Hydrogen peroxide (H₂O₂) is considered an environmentally friendly chemical that can be used as a pulp bleaching agent, for example, or as a green and selective oxidant for many different chemical reaction processes; its only byproduct is water. The industry currently produces highly concentrated H₂O₂ in large-scale plants at central locations worldwide using the anthraquinone process – an energy-intensive and cost-intensive process.

PROCESS 1: ELECTRICITY TO CREATE H₂O₂

Many users want to avoid costly storage and security logistics; they would prefer to produce H₂O₂ locally on demand and use it immediately. A process has been developed for electrochemical production of H₂O₂ in an aqueous reaction system (both cathodic and anodic), including coupling it to subsequent chemical processes. H₂O₂ is produced continuously, which allows for immediate forward integration in the form of prepared aqueous solutions. The process can take place locally and on a small scale, and under ideal conditions it uses 100 percent renewable energy. It includes upstream processing (providing reactants, electricity, and auxiliary agents), the electrochemical cell with a catalyst and a gas diffusion electrode as a central reactor unit for H₂O₂ synthesis, downstream processing (H₂O₂ with the required product purity and concentration) as well as a connection to the subsequent chemical processes (selective oxidation, demonstrated here using the example of fuel desulfurization).

The "Electricity to create H₂O₂" process has created the following innovative solutions for industrial applications:

- Catalyst systems for cathodic H₂O₂ synthesis
- Diamond electrodes for anodic H₂O₂ synthesis
- Electrode, cell, and stack designs
- Innovative ion-conducting membranes with low fluorine content and high ionic conductivity
- Real-time-capable process analytics
- Continuous separation and concentration processes
- Application examples for chemical synthesis, material processing, and hygiene/purification

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CO₂ REFINERY I

Carbon dioxide (CO₂) is produced worldwide using industrial processes. It is a useful carbon source for chemicals and fuels if renewable energy is used to activate it. Where this is possible, electricity, CO₂, and water can be used as raw materials for an innovative CO₂ refinery.

3 Test facility for demonstrating electrochemical ethene production.

PROCESS 2: ELECTRICITY TO CREATE ETHENE

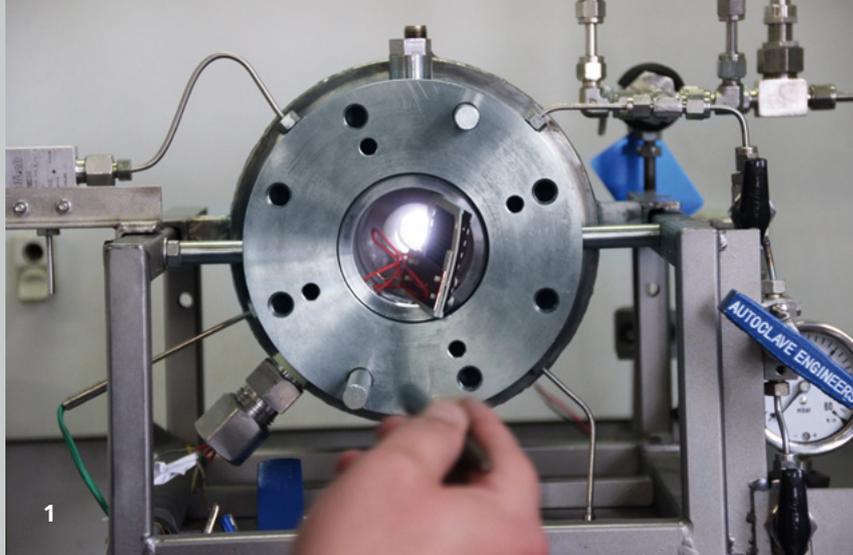
Ethene is by far the most important basic chemical used in the petrochemical industry; nearly 60 percent of it is used as a raw material for the mass plastic polyethylene (PE). Like all alkenes, ethene is currently made from petroleum. In this lighthouse project, researchers were able to demonstrate the success of a continuous electrochemical process to produce ethene from CO₂ and water. In order to achieve this, they used various procedures to create and validate copper-based catalysts, and placed them on gas diffusion electrodes (GDEs). GDEs are electrodes in which the three aggregate states – solid (catalyst), liquid (H₂O) and gas (CO₂) – remain in contact with one another so that an electrochemical reaction can take place in the catalyst between the liquid and gaseous phase. In order to achieve high yields, the researchers not only optimized the catalysts and the GDE, but also built a demonstrator in which electrodes measuring up to 130 cm² can be tested in continuous operation and process parameters can be optimized. It is the first demonstrator that can be used to show an industry-oriented process and for studying scaling effects.

The "Electricity to create ethene" process thus provides the following innovative solutions for industrial applications:

- Producing copper-based and metal-free catalysts for synthesizing ethene (deep eutectic solvent, co-precipitation, electrochemical deposition)
- Manufacturing metallic capillary electrodes and electrochemical reactor modules
- Automated demonstrator for testing electrochemical synthesis processes and catalysts during continuous operation (electrode size: 130 cm²)

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CO₂ REFINERY II

1 Reactor for high-pressure electrolysis of CO₂.

Alcohols are an important group of substances because they serve as the starting material for many chemical processes. Two different electrochemical processes were developed for producing alcohols (C₁-C₄ alcohols, C₄-C₂₀ alcohols¹) from CO₂. In single-step high-pressure electrolysis, CO₂ occurs as a continuous phase for which additional reactants are dosed. In the two-step process, co-electrolysis is first used to generate synthetic gas at high temperatures; during the second step, the gas continues to react and becomes long-chain molecules.

PROCESS 3: SINGLE STEP WITH ELECTRICITY TO CREATE ALCOHOLS AND ACIDS

Short-chain C₁-C₄ alcohols are basic chemicals used by the chemical industry. The C₁ alcohol methanol, for example, is further processed to create formaldehyde, acetic acid, methyl tertiary butyl ether (MTBE), methyl methacrylate, methyl chloride, and methylamines. There are currently more than 100 commercial methanol plants in use, with a total capacity of 80 million tonne per year. A new single-step high-pressure electrolysis process was developed that produces methanol and C₂-C₄ alcohols from CO₂ and water. In this process, CO₂ is not dissolved in water; instead, water is dissolved under pressure in supercritical CO₂. The innovation here is that the alcohols are produced in a single process step by directly reducing CO₂. The electrochemical reduction of supercritical CO₂ has clear advantages over using CO₂ in water, such as shifting the phase balance and achieving higher yields.

The "Single step with electricity" process provides the following innovative solutions for industrial applications:

- Catalyst preparation up to kg scale
- Continuous manufacturing of electrodes up to 50 cm wide
- Surface coating of electrodes with catalytically active material, using a spray process
- High-pressure reactors for electrosynthesis (40 ml to 2 l; 150 bar) including online gas chromatography
- Process with high CO₂ conversion rates that avoids hydrogen formation

¹ The number in the index describes the number of carbon atoms found in the alcohol (symbol: "C")

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2 Reactor for producing long-chain alcohols using the Fischer-Tropsch process.

PROCESS 4: TWO STEPS WITH ELECTRICITY TO CREATE LONG-CHAIN ALCOHOLS

Long-chain alcohols are used for producing plastics, cosmetics and laundry detergents and also as fuel additives. Because of their advantageous properties, higher alcohols are expensive to use as raw materials. A coupled process involving high-temperature electrolysis (solid oxide electrolysis cell – SOEC) and Fischer-Tropsch synthesis was developed for producing long-chain alcohols (C₄-C₂₀) from CO₂ and water. The innovation here is that it is the first time such a synthesis has been technically realized using a two-step electrolysis-based process. CO₂ activation takes place right away in the SOEC. New, cost-effective iron-based catalysts and a new reactor were developed for alcohol synthesis, which moves the product spectrum further toward long-chain alcohols.

The "Two steps with SOEC and Fischer-Tropsch synthesis" process makes the following innovative solutions available for industrial applications:

- Highly durable SOEC modules optimized for co-electrolysis, used for producing synthetic gas
- Iron-based catalysts, carrier concepts and reactors for Fischer-Tropsch synthesis to create long-chain alcohols
- Process development for sustainable synthesis processes
- Scale-up to demonstration scale

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INNOVATIVE HELPERS

1 An innovative membrane for divided electrochemical cells: high-performance, cost-effective, and environmentally friendly.

2 Diamond electrodes for anodic H_2O_2 production.

3 Quality assurance experiments.

Membranes and electrodes are basic components of electrochemical cells, and clever analytics are an important tool for creating reliable, efficient and sustainable processes. A series of characterization processes is now available specifically for electrochemical production.

CHARACTERIZATION OF ELECTROCHEMICAL COMPONENTS

Membrane development for divided electrochemical cells

The class of polyphenyl quinoxalines was chosen as the basis for developing the membranes. They have excellent thermo-oxidative and chemical stability. Polycondensation reactions have been successfully performed to create the polyphenyl quinoxalines and for sulfonating as well as quaternizing them, and cost-effective fluorine-reduced membranes have been manufactured.

Electrode development (e.g. diamond electrodes for anodic H_2O_2 production)

Diamond electrodes were manufactured using hot-wire CVD (chemical vapor deposition), and a reactor structure was built that permitted the direct anodic production of H_2O_2 .

Electrochemical analytics and quality assurance

In the course of the project, systematic analysis procedures were developed in order to study and evaluate electrochemical components. These include an aging test, material characterization methods and benchmark analyses.

The "Characterization of electrochemical components" area provides the following innovative solutions for industrial applications:

- Characterizing innovative ion-conducting membranes with low fluorine content
- Electrochemical test cells for quality assurance in electrodes and membranes
- Aging test to evaluate long-term durability of electrochemical components
- Damage analyses of electrochemical components

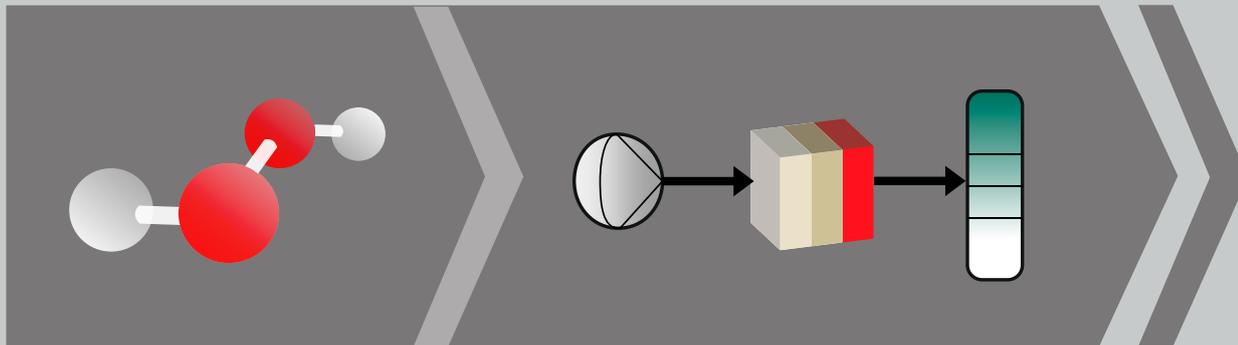
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FROM MOLECULE TO PROCESS

Mathematical equations describe mechanisms and connections from the "molecule" level to the "process" level. In this lighthouse project, researchers are using these equations to develop a software tool for model-based decision-making support in order to achieve more cost-effective, efficient, and sustainable designs and operations for electrochemical processes.

4 *Modeling, simulation, and optimization on various scales.*

PROCESS MODELING, SIMULATION AND OPTIMIZATION

Modeling, simulation and optimization take place on three levels:

- Modeling of the catalyzed electrochemical reaction with adjustments to the reaction parameters
- Modeling of electrochemical cells
- Modeling of overall processes

For this process, a high product yield must be achieved with as little total output as possible. Both values depend on the design of the flow diagram and the chosen operating point. Because individual target functions compete with each other, this creates a multi-criteria optimization problem. An interactive decision support tool for multidimensional data sets helps visualize the results and control the electrochemical processes according to the energy market.

The "Process modeling, simulation, and optimization" area provides the following innovative solutions for industrial applications:

- Expanded methodology for evaluating RRDE¹ experiments
- Independent Aspen module for mapping electrochemical cells
- Coupling of the Aspen simulation with multi-criteria optimization and sustainability analysis
- Software, including a graphic interface, for decision support during electrosynthesis

¹ RRDE: **R**otating **r**ing **d**isc **e**lectrode

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FROM PROCESS TO SYSTEM

1 *Dr. Markus Hiebel in
consultation with stakeholders.*

The concept of "Electricity as a resource" only makes sense when the processes and components on the whole become a functioning system that offers advantages for production. Energy scenarios, the connection of energy and production systems, sustainability analyses, and stakeholder participation are important elements.

SYSTEM ANALYSIS AND SUSTAINABILITY ASSESSMENT

Trends and developments in the energy system were used to derive scenarios for the future electricity mix and electricity pricing. Together with scenarios for Germany as an economic system, they provide the basis for a comparative sustainability analysis that includes an economic process evaluation. An integrated sustainability concept offers strategic decision support during process development. In order to interpret the results, researchers developed participation concepts and held discussions with stakeholders. The findings from connecting the electrochemical production processes to the energy system reveal the opportunities and limits of this new approach.

The "System analysis and sustainability assessment" area provides the following innovative solutions for industrial applications:

- Consulting services for linking the energy and production systems
- Creating customized maps for CO₂ logistics
- Decision support for location planning
- Life cycle and sustainability assessments for process technologies in the early stages of development
- New formats for integrating stakeholders into process innovations

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BENEFITS THROUGH NETWORKING

BUSINESS AND INNOVATION CENTER BIC

In order to harness the potential of electrochemistry as well as the potential of electricity and CO₂ as raw materials, basic knowledge must be combined with application knowledge as well as with the associated markets and sustainable recycling chains. Fraunhofer has established a new platform concept for the "Electricity as a resource" application: the Business and Innovation Center (BIC). On this platform, researchers work with marketing experts and business development managers in various sectors to design industry-relevant services.

The Business and Innovation Center provides R&D services for industry and society, and acts as a nucleus and technology center for spin-offs. The result is Fraunhofer's "eSource®" brand universe, which combines all of its competences, products, processes and services involving electrochemistry.

We will be happy to work with you to help develop your project. You can count on our expertise in:

- Process development, construction, and operation of pilot plants (batch and continuous operation)
- Developing and testing (electro-) catalysts, cells, and stacks
- Procedures for manufacturing and testing electrodes for electrochemical processes
- Developing ion-conducting polymer membranes
- Analyzing and characterizing catalysts, electrodes, cells, and membranes
- Modeling, simulation, and optimization
- System analysis and sustainability assessment
- Innovation management
- Project and business model development

Visit our platform online: www.electricity-as-a-resource.de

We look forward to your questions, requests, and ideas for collaborative innovations.

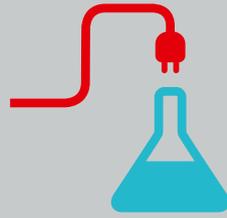


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2 "Electricity as a resource" depends on teamwork and extensive networking.

ELECTRICITY AS A RESOURCE



LIGHTHOUSE PROJECT: ELECTRICITY AS A RESOURCE

The lighthouse project "Electricity as a resource" was supported by funds from the Fraunhofer-Gesellschaft. The goal of Fraunhofer's lighthouse projects is to exploit Fraunhofer's synergy potential by pooling the expertise of multiple Fraunhofer institutes in order to deliver solutions for the challenges of German industry. The participating institutes are grateful for the generous support.

Project term

August 2015 – July 2018

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