DECHEMA
FORSCHUNGSINSTITUT
Stiftung bürgerlichen Rechts

Electrochemistry

Research Activities 2017

Preface

DECHEMA-Forschungsinstitut
Interdisciplinary Research for Sustainable Technologies

The DECHEMA-Forschungsinstitut (DFI) stands at the forefront of interdisciplinary research for sustainable materials, processes and products for the industrialized society. It is a scientific research center where chemists, engineers and biotechnologists jointly work on creating novel concepts and innovative interdisciplinary solutions based on materials science, chemical engineering and biotechnology.

The institute has a staff of approx. 80 who are involved in

- Basic and preindustrial **research** in Chemical Engineering, Biotechnology, Environmental Technology, and Materials Sciences
- **Teaching activities** at German universities in the fields mentioned above
- **Continuing professional development** courses for participants from industry and universities
- Development of solutions to **industrial problems**
- **Scientific support** for DECHEMA working parties and conferences

The structure of the institute is undoubtedly unique in Germany: based on the competencies of five academic research groups:

- High Temperature Materials
- Corrosion
- Electrochemistry
- Chemical Technology
- Industrial Biotechnology

These groups, together with additional service units, strive for novel ideas and scientific concepts to target the needs of our industrialized society.
It focuses on three main areas of research, covering the whole spectrum from fundamental aspects to application:

- Energy Efficiency
  Fuel Cells
  Metal-Air-Batteries and other energy storage systems
  Photocatalytic Systems
- Conservation of Resources
  Innovative Corrosion Protection Systems
  Recycling of precious metals
  Water Treatment

- Biotech for Chemical Production
  Utilization of Renewable Resources
  Biotechnological Production Routes for Chemical Products

Driven by the needs of HiTech industries in the fields of biotechnology, materials, and chemical engineering and other industrial areas including energy conversion, automotive and aircraft technologies, the research activities at the DECHEMA-Forschungsinstitut cover the whole spectrum from fundamental aspects to application.

These activities reflect the institute's commitment to bridging the gap between academia and industry in the scientific and technological fields represented by DECHEMA.

Fields of expertise at the DECHEMA-Forschungsinstitut are:

- High temperature materials
- Corrosion protection in extremely aggressive environments
- Development of novel coating systems
- Advanced investigation methods for high temperature corrosion
- Nanoparticle-based coatings
- Modification of anodic oxide layers
- High resolution methods for corrosion investigations
- Microbially influenced corrosion
- Redox-flow batteries
- Metal-air energy storage systems
- Fuel cells
- Reaction engineering
- Photocatalysis
- Functional surfaces
- Molecular electrochemistry
- Electrochemical water treatment
- Bioelectrochemistry
- Bioprocess development
- Enzymatic catalysis and microbial syntheses of fine chemicals
- Metabolic engineering of microorganisms for industrial production

Every year, we publish five *Research Activities* brochures, each presenting one research group.

For more information about the DECHEMA-Forschungsinstitut, please visit: www.dechema-dfi.de

Contents

Electrochemistry Group - Overview

Research Fields

- **Electrochemical water treatment:**
  elimination of micro-pollutants by electrosorption and/or electrochemical oxidation, selective adsorption and desorption of organic molecules at carbon based electrodes, disinfection, desalination, electrochemical water softening, development of new reactors: a packed bed combined with a stack reactor and a fluidized bed electrode composed of magnetic and electron conducting particles combined with an electromagnetic field, closing of material cycles in industrial processes, electrochemical synthesis of oxidizing substances, electrochemical dehalogenation of persistent compounds, e. g. radio-opaque substances.
- **Molecular electrochemistry:**
  electrochemical synthesis of organic compounds, electroorganic synthesis will be expanded within the next years, microbial electrosynthesis combining bacteria with electrochemical methods.
- **Electrochemical energy storage and transformation:**
  redox-flow batteries, study of stability and degradation mechanisms, lifetime prognosis, characterization of new electrode materials and new electrode geometries, e. g. tubular cells, membranes and electrolytes, development of new electrolytes, establishing and coordination of a national redox-flow network.

Methods

- **Conventional electrochemical techniques, e.g.:**
  Stationary current-potential curves, cyclic voltammetry, electrochemical impedance spectroscopy, chronoamperometry, rotating disc and ring-disc electrodes, galvanostatic or potentiostatic polarization.
- **In situ combination methods:**
  Spectroelectrochemistry (UV-Vis-NIR), Fluorescence microscopy with spatially-resolved Vis-spectroscopy, electrochemical quartz crystal microbalance, in-house development of electrochemical cells.
- **Non electrochemical analytical methods:**
  FT-IR-spectroscopy, Atomic absorption spectroscopy, Ion chromatography (anions and cations), Gas chromatography (detectors: TCD, FID, ECD), High-performance liquid chromatography (UV/Vis), Contact angle measurement.

Research Projects 2017

DegraBat - Degradation processes in All-Vanadium-Redox-Flow-Batteries

Period: 01. 06.2017 - 31.05.2020

Partners: Fraunhofer-Institut für Chemische Technologie
Karlsruher Institut für Technologie KIT
Freie Universität Berlin
SGL Carbon SE
FUMATECH BWT GmbH
balticFuelCells GmbH
AMG TITANIUM ALLOYS & COATINGS
GfE Gesellschaft für Elektrometallurgie mbH
DKE VDE

Funders: BMEL

Motivation:

The Vanadium rdox-flow-battery is a promising technology for renewable energy storage. Advantages are the independent scalability of power (cell/stack) and capacity (tank), low self-discharge and long service life. However, degradation of the battery components (electrodes, membrane, electrolyte, sealing) causes losses in capacity and power and shorter lifetime of the battery.

Summary:

Within this joint project the degradation processes of components in vanadium redox-flow-batteries will be investigated and shall be predicted.

The aims are:

- Identification and characterization of degradation mechanisms
- Evaluation of methods and routines for accelerated degradation of the battery components
- Development of a model for state of health analysis and lifetime prognosis

Degradation mechanism will be characterized qualitatively and quantitatively in relation to different parameters such as operation time, charge/discharge behavior, and surrounding conditions. For this, each battery components (membrane, electrode/bipolar plate, electrolyte, sealing) will be studied with different analysis methods. Special interest of the working group Electrochemistry group will be focused on the degradation processes of the vanadium electrolyte. Main task is to develop and establish easy-to-apply and effective online-monitoring methods in order to precisely diagnose the state of charge (SoC) and state of health (SoH) of redox-flow-battery.
Furthermore within the project, methods and routines which allow a targeted and accelerated degradation of the battery components will be developed and established. Finally, a degradation model will be newly developed. This model shall allow prognosis of lifetime and contribute to longer service life of vanadium redox-flow-batteries.

Gefördert durch:

Bundesministerium
für Ernährung
und Landwirtschaft

aufgrund eines Beschlusses
des Deutschen Bundestages

ElektroWirbel – Closing of material cycles of industrial Processes by Development of new packed and fluidized electrodes

Period: 01.09.2016 - 31.08.2019

Partners: Covestro Deutschland AG, Leverkusen, Deutschland
Evonik Industries AG
FuMA-Tech GmbH
Fraunhofer ISC-IWKS
KIT Karlsruhe
DWI Leibniz-Institut für interaktive Materialien

Funder: BMBF

The electrochemical stirred reactor systems on the basis of magnetic particles represent a new reactor concept by which it should be possible to purify industrial waste water containing organic residues effectively, sustainably and economically.

The innovation consists of the first time combination of a magnetically stirred reactor with electrochemical polarization.

The main aims of the project are:

- Design of a laboratory reactor cell with 3-electrode assembly which enables the operation of the reactor in a continuous flow.
- Desalination of waste water with low salinity
- Potential driven adsorption of organics onto the magnetic particles by varying the operation parameters.
- Regeneration of the magnetic particles
- Endurance tests to study the stability of the particles and elucidation of deterioration mechanism.
- Conception and Operation of the demonstrators at the location of the industrial partners

The successful development of an electrochemical magnetically stirred reactor opens up various applications, for example microbiological electrosynthesis, water softening, treatment of particle and/or fiber containing medias, electro organic synthesis, processing brackish water, elimination of trace substances in sewage plants or the recovery of valuable materials like heavy metal ions out of process waste water.

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tubulAir± Project part: Quality analysis of components

Period: 01.09.2012 - 31.12.2017

Partners: Hochschule für Angewandte Wissenschaften Hamburg (HAW)
Universität Hamburg
FAU Erlangen-Nürnberg
DWI an der RWTH Aachen
FuMA-Tech GmbH
Uniwell Rohrsysteme GmbH & Co. KG
JRC-IET

Funder: BMBF

Target of the project tubulAir± is the development of a tubular Vanadium-air redox-flow battery with increased energy and power density for stationary appliances. To achieve this, the fluid electrolyte of the VRB on the cathode shall be replaced by an air/water steam electrode. Thus the energy density might basically be doubled compared to a VRB. To achieve a better cost effectiveness, a micro tubular cell structure will be developed.

Within the frame of this project the electrochemistry is working as a connective link between manufacturers of the single components (electrolyte, electrode, catalyst, membrane) and users of the redox-flow system. Analysis of the efficiency and stability of the components will be carried out by the electrochemistry group and the single components as well as their joint action will be characterized.

Special interest will be gained on the stability of the components under relevant conditions.

The scientific findings will be assembled to a catalogue of requirements for quality of redox-flow-batteries and their electrodes, membranes and electrolytes.

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Radar - Wastewater Treatment with Radicals: Development of an Electrochemical Module for the production of oxidants for Wastewater Treatment

Period: 01.04.2017 - 31.03.2020

Partners: Eisenhuth GmbH & Co. KG
Evac GmbH
Technische Universität Clausthal
Clausthaler Umwelttechnik-Institut GmbH (CUTEC)
CONDIAS GmbH
Covestro Deutschland AG
Eilenburger Elektrolyse-und Umwelttechnik GmbH

Funders: BMBF

Objective

The cornerstones of sustainable water management are a resource-conserving handling of natural waters and the prevention of further pollution. Poorly degradable organics in treated wastewater are a major challenge for environmentally friendly water management. The reuse of process water in industrial water cycles requires removal of interfering organic residues. In municipal sewage treatment plants, poorly degradable organic residues, e.g. pharmaceuticals, are inadequately eliminated and discarded into the aquatic environment.

Approach to remove persistent organic compounds from wastewater

In the BMBF-funded project RADAR, the persistent organic matter is largely mineralized by OH radicals. The electrochemical module for generating the OH radicals consists of a novel electrode combination of boron-doped diamond electrode (OH radicals / ozone) and gas diffusion electrode (hydrogen peroxide). High oxidative species are generated at both electrodes and can thus be added directly or indirectly to the wastewater for oxidation. In this way, the current efficiency and the efficiency of the wastewater treatment are increased.
The subject of the investigation is to design a scalable design of the electrochemical module. In advance, the properties of the individual electrodes are examined in a laboratory scale cell in order to coordinate their operation at their optimum. Moreover, the degradation of persistent model molecules in terms of high degradation rates and current efficiency as well as oxidation by-products will be investigated.

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Re-Salt - Recycling of industrial process water

Period:	01.10.2016 - 31.09.2019
Partners:	Covestro Deutschalnd AG Donau Carbon GmbH Anwendungstechnik EnviroChemie GmbH SolarSpring GmbH membrane solutions Technology Arts Science TH Köln TZW Technologiezentrum Wasser Universität Duisburg-Essen
Funders:	BMBF

Nowadays water counts as a limited and valuable resource and the environmentally friendly recovery of process wastewater has to be considered as an indispensable issue. Re-salt (**Re**cycling of industrial **salt**-laden process water) is funded by the German Federal Ministry of Education and Researche (BMBF) with the government's funding initiative WavE. This joint project is focusing on salt-laden pollutants from the chemical industry and aims at the elimination of harmful organic molecules and the re-concentration of sodium chloride in the recovered process water. This approach would allow a recirculation of the remaining sodium chloride into the chlor-alkali electrolysis, the most important industrial process to produce chlorine. However, as a part of Re-salt the DFI focusses on the removal of organic-based pollutants in the effluents. Since it is known that electrosorption can be a powerful tool for wastewater treatment the idea to accelerate and enhance adsorption with polarization of a conductive carbon-based adsorber seemed likely. Furthermore, this concept allows a regeneration of the adsorber bed due to reversion of polarity.

To realize this concept filter-press-cell consisting off a membrane, two graphite sheets as electrical contacts and two chambers filled with adsorber was designed. A range of parameters, pH-dependency, electrolyte and potential, will be tested to realize an economic adsoption/desorption process.

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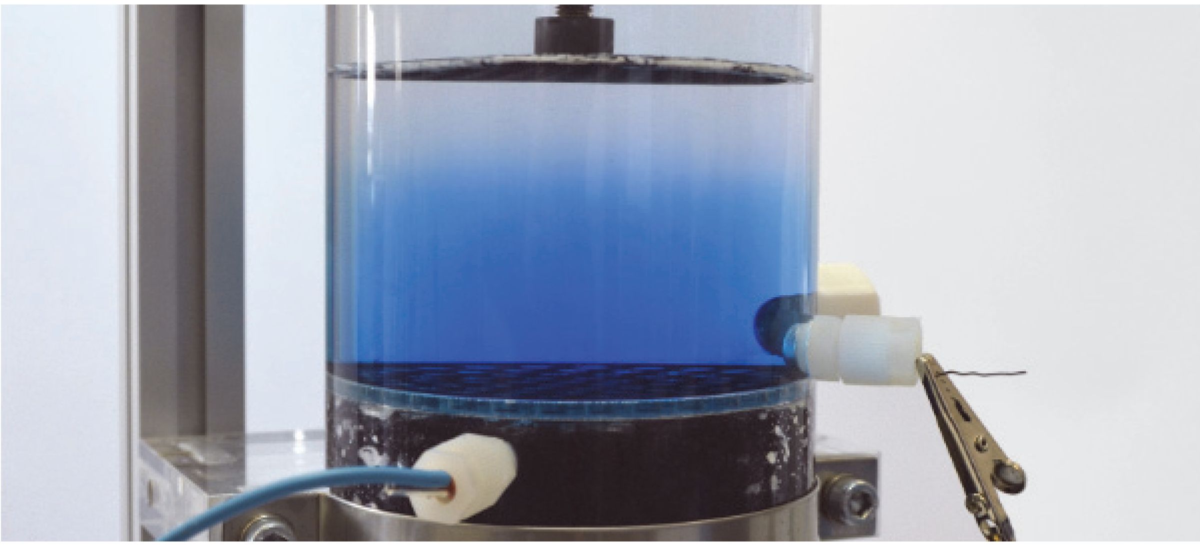
ZellCoDia - A new combination of diamond and oxygen diffusion electrodes



Period: 01.04.2017 - 31.03.2020

Partners: CONDIAS GmbH, Itzehoe, Deutschland
Covestro Deutschland AG, Leverkusen, Deutschland
Eilenburger Elektrolyse- und Umwelttechnik GmbH, Eilenburg, Deutschland
Johannes Gutenberg Universität Mainz, Mainz, Deutschland

Funders: BMBF

The chemical industry is mainly based on classical synthesis processes although electrochemical processes can shorten synthesis routes. In the context of the energy revolution resource-conserving alternatives are important. A benefit of electrochemical processes is that special chemicals like oxidizing and reducing agents are not necessary. In combination with shorter synthesis routes a more eco-friendly, energy-saving and cost-efficient process can be developed. However, as a consequence for lack of robust and user-friendly electrolysis cells, the electro-organic synthesis is still a niche technology.

ZellCoDia aims at the development of two new cells for the electro synthesis. A special point is the new combination of gas-diffusion electrodes and boron-doped diamond electrodes.

Within the frame of this project the electrochemistry group focuses on a cell for poor conducting electrolytes. An electrochemical on-site technology has to be developed, which offers new ways for the generation of hazardous products from uncritical starting materials economically, e.g. the synthesis of peracetic acid.

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Microbial Electrosynthesis - Research project on the evaluation of usage of electric energy for future microbial production processes

Period: 01.03.2013 - 28.02.2018

Partner: Industrial Biotechnology Group at DFI

Funder: BMBF

Microbial electrosynthesis (MES) make use of the endogenous property of some microorganisms to interact with electrodes. It can be defined as an electricity-driven or electricity-influenced microbial product synthesis. The project covers the investigation, evaluation and the extension of microbial electrosynthesis for biotechnological production. The main aims of the project are:

- Immobilization of electroactive bacteria on different electrode materials
- Application of wild-type strains for microbial electrosynthesis
- Establishment of electrochemical methods (e.g. electrochemical impedance spectroscopy) for the detection of biofilm formation
- Development of scalable reactor systems
- Microbial electrosynthesis using molecular optimized microbial strains

Immobilization of electroactive bacteria and monitoring of the subsequent biofilm formation on electrode surfaces are one of the major challenges towards industrial application of MES.

In this project, a flow cell for the simultaneous detection of electroactive biofilms with impedance spectroscopy and confocal laser scanning microscopy was developed.

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Selected publications

M. Stöckl, C. Schlegel, A. Sydow, D. Holtmann, R. Ulber, K-M. Mangold

Membrane Separated Flow Cell for Parallelized Electrochemical Impedance Spectroscopy and Confocal Laser Scanning Microscopy to Characterize Electro-Active Microorganisms

Electrochimica Acta 220 (2016) 440-452

Understanding the attachment of electro-active bacteria to electrode surfaces and their subsequent biofilm formation is one of the major challenges for the establishment of bacterial bioelectrochemial systems (BES). For a constant observation of biofilm growth, providing information on different stages of biofilm formation, continuous monitoring methods are required. In this paper a combination of two powerful analytical methods, Electrochemical Impedance Spectroscopy (EIS) and Confocal Laser Scanning Microscopy (CLSM), for biofilm monitoring is presented. A custom-built flow cell with a transparent indium tin oxide working electrode (WE) was constructed allowing monitoring of cell attachment to a working electrode simultaneously by EIS and CLSM. Cyclic Voltammetry (CV) and EIS of an iron (II)/iron (III) redox couple indicate that the flow cell is suitable for electrochemical experiments. An engineered Shewanella oneidensis MR-1 (ATCC700550) producing eGFP was used as electro-active model organism to demonstrate the practical application of the flow cell as BES to monitor cell attachment simultaneously with EIS and CLSM. Applying the flow cell as MFC (transparent working electrode poised as anode) produced a typical current curve for such a system. From the equivalent circuit used to interpret EIS data the charge transfer resistance RCT is sensitive to attachment of microorganisms. Fitted RCT was increased initially after cell inoculation and then lowered constantly with progressing experimental time. In parallel taken CLSM images show that bacteria already adhered to the WE 5 min after inoculation. A mono- respectively bilayer of electro-active cells was observed after 17 h on the WE surface. With the presented flow cell interpretation of EIS measurements is significantly improved by simultaneous CLSM imaging, leading to a wide range of attachment information and pointing to the investigation of less studied and less established electro-active bacteria.

C. Weidlich, V. Greb, P. Fröhlich, M. Bertau, K.-M. Mangold
„Recovering Inorganic Resources by Applying Boron-Doped Diamond Electrodes"
Chemie Ingenieur Technik 89 (1-2) (2017) 188-193

Due to limited primary deposits and simultaneously increasing demand for various metals, the use of secondary raw materials is becoming increasingly important. With a new electrochemical method metals, e.g., copper, zinc, and nickel, can be dissolved and recovered from waste like ashes, slags, and spoil banks. Significant improvement of the dissolution of the metals is achieved by in situ production of peracids from mineral acids using boron-doped diamond electrodes.

K.-M. Mangold, J. Schuster, C. Weidlich
Synthesis and properties of magnetite/polypyrrole core-shell nanocomposites and polypyrrole hollow spheres
Electrochimica Acta 56 (2011) 3616-3619

ABSTRACT
In this work a new route for preparation of core–shell nanoparticles composed of an iron oxide core and a polypyrrole (PPy) shell is explored. During the preparation procedure the initially formed iron(0) core is converted to magnetite. It is demonstrated, that the magnetite cores can completely be dissolved by reaction with acid. Furthermore the dissolution of iron oxide cores by electrolysis also is possible. The resulting PPy hollow spheres as well as the core–shell nanocomposites are electrochemically active.

For further information, also to completed projects or about the DECHEMA-Forschungsinstitut, please visit: www.dechema-dfi.de

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