



DECHEMA

FORSCHUNGSINSTITUT

Stiftung bürgerlichen Rechts

Chemical Technology

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

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Chemical Technology Group - Overview

The demand for chemical products is growing at an exponential rate. This tremendous challenge can be met by substantially improving existing strategies and optimizing processes in chemical plants. In the past decade, great effort was required to match production efficiency to the needs of the society in view of product selectivity, material and energy costs, as well as environmental protection. In this context, Chemical Technology is a major contributor, transferring fundamental research to improvements and innovation.

The key research topics of the group are:

- Photocatalysis
- Reaction engineering
- Sustainable production
- Air-, water- and surface cleaning
- Electrochemical energy storage and conversion.

Current Photocatalysis Research

The main research focus of the chemical technology group at the DFI is the integration of photocatalysis into chemical, electrochemical and biochemical processes. The advantage of photocatalysis lies in the ease of supplying energy in form of photons which is reagent-, contact- and residue-free. Also, clever selection of reactants allows photocatalytic reactions to realize several consecutive reaction steps in a one-pot-synthesis. Also, if sunlight is used as the energy source to drive the photocatalytic reaction, the process becomes cheaper, sustainable and CO₂-neutral as sunlight is available free of charge and without a carbon footprint.

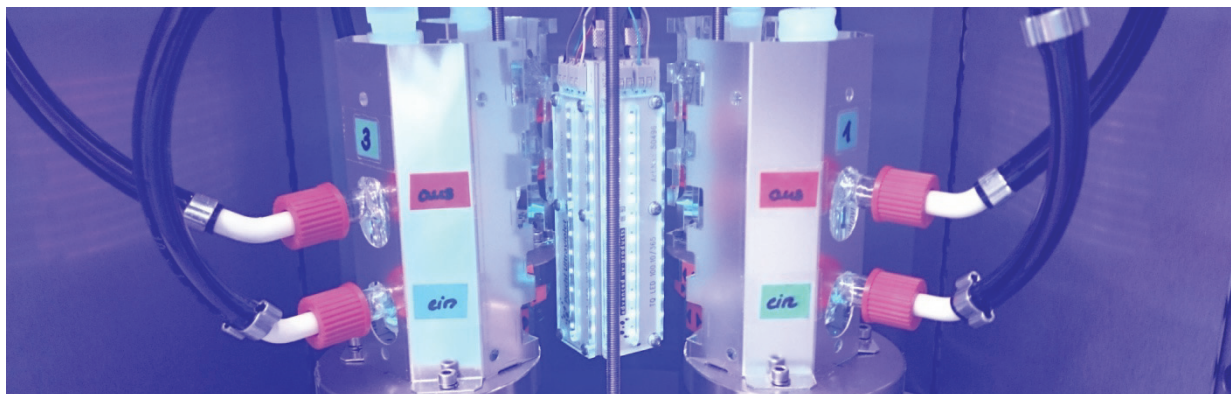
In addition to their uses in synthetic applications the group also explores the oxidative powers of photocatalysts for the abatement of undesired contaminants. Due to the immense oxidation potential of most photocatalysts, *e.g.* titanium dioxide, these materials are able to mineralize virtually all organic compounds when illuminated with light. This property can be used in water remediation and air pollution cleaning as well as to create actively self-cleaning and self-sterilizing surfaces. The group is involved in the development of more efficient and selective photocatalysts as well as improved coating techniques.

Current Energy research

Furthermore, polymer electrolyte membrane and solid oxide fuel cell technology as well as metal/air batteries are being investigated. The group developed gas diffusion electrodes and catalysts for these applications and electrochemically characterizes them under half-cell and fuel-cell conditions. Also, demonstrators are tested under practical conditions. Project examples are a charger unit based on a direct methanol fuel cell (DMFC), a rechargeable zinc/air battery and a hydrogen and methanol mid-temperature fuel cell.

Research Projects 2017

Photocatalytic quinoline production from nitroaromatic compounds (QuinoLight)



Period: 01.01.2016 - 31.12.2018

Partners: Justus-Liebig-Universität Gießen,
Physikalisch-Chemisches Institut, Research Group Marschall (JLU)
Universität Stuttgart, Institut für Technische Chemie,
Research Group Ziegenbalg (ITC)

Funder: AiF

Heterogeneous photocatalysis has been known for a long time mainly for its applications in the degradation of organic impurities and photocatalytic water splitting. However, especially in recent years, photocatalytic reactions have also become an important field in organic synthesis. The irradiation of semiconductors with light of a suitable wavelength produces very reactive states, so called electron-hole pairs, which can be used for a variety of chemical reactions such as oxidations, reductions or C-C couplings.

Using the example reaction of the quinoline synthesis (Figure 1) two important aspects for the development of photocatalysis are addressed in the present research project. On one side, improved and optimized photocatalysts for organic synthesis will be developed and on the other side a scalable photoreactor concept in which the process can be operated continuously is planned. The results should be applicable not only for the selected target reaction, but also for other heterogeneous photocatalytic reactions.

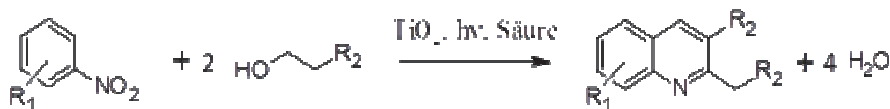


Figure 1: Photocatalytic quinoline synthesis from nitroaromatics and alcohols.

The work program is handled by three research partners:

At Justus-Liebig-Universität Giessen (JLU), the research group Marschall works on the further development of photocatalysts. The typically used titanium dioxide has a very high oxidation potential that can lead to undesirable side reactions and in some cases mineralize part of the substrate. In addition, it can only be excited by high-energy UVA light. Therefore, attempts should be made here to use photocatalysts based on other materials which have a significantly milder oxidation potential and can already be excited with visible light.

At DECHEMA-Forschungsinstitut (DFI), kinetics studies are used to investigate and optimize the reaction behavior. Previous laboratory tests have achieved conversions of up to 54%. By varying stoichiometry, light intensity and temperature the reaction should be further optimized with regard to conversion and selectivity. The reaction is to be operated as a continuous process. In addition, the use of substituted educts is intended to further explore the spectrum of accessible products.

Photoreactor development is carried out at the research group Ziegenbalg, Institute for Technical Chemistry (ITC) of the University of Stuttgart. Various photoreactor concepts are to be investigated and quickly evaluated using rapid prototyping. Both the approach in which the photocatalyst particles are suspended in the reaction medium and those in which they are immobilized on the walls of the photoreactor are tested and compared.

Supported by:



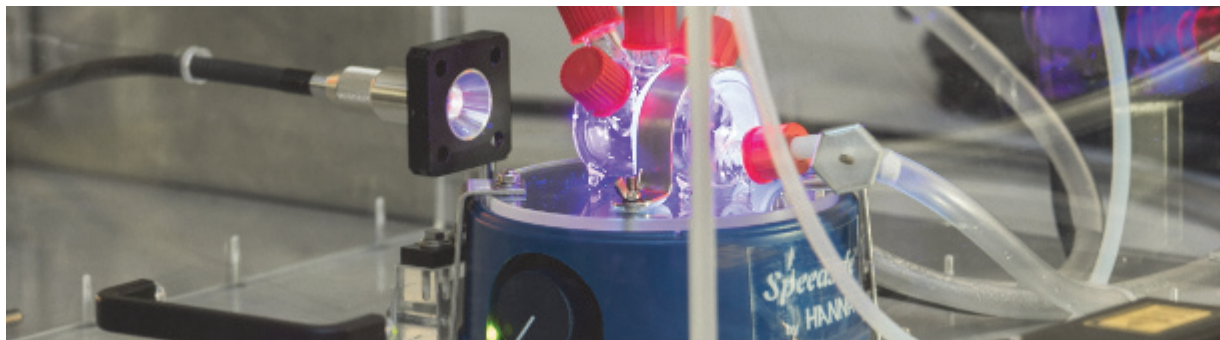
Federal Ministry
for Economic Affairs
and Energy

on the basis of a decision
by the German Bundestag

Das IGF-Vorhaben Nr. 18904 N-1 der Forschungsvereinigung DECHEMA e.V., Theodor-Heuss-Allee 25, 60486 Frankfurt am Main wurde über die AiF im Rahmen des Programms zur Förderung der industriellen Gemeinschaftsforschung (IGF) vom Bundesministerium für Wirtschaft und Energie aufgrund eines Beschlusses des Deutschen Bundestages gefördert.



Photocatalytic in situ hydrogen peroxide production for biocatalysis based on peroxidases



Period: 01.09.2015 - 31.08.2018

Funder: Deutsche Forschungsgemeinschaft (DFG)

The use of enzymes such as oxidoreductases in organic synthesis offers highly selective, efficient and therefore sustainable chemical processes. However, industrial utilization of oxidoreductases is often limited by their requirement of expensive cofactors. Peroxidases have the advantage that their cofactor, hydrogen peroxide, is economically priced and can be easily synthesized. The challenge for utilization of peroxidases is their poor stability against their own cofactor, hydrogen peroxide.

The aim of the project is to provide the peroxidase with ideal and therefore mild concentration of hydrogen peroxide to raise the stability of the enzyme and thereby TTN (total turnover number) of the reaction. For this purpose, the photocatalytic generation of hydrogen peroxide by titanium dioxide and other photocatalysts will be explored and optimized under different conditions. Afterwards, this process will be combined with the Peroxidase to form an integrated photobiocatalytic process, *cf.* Figure 1.

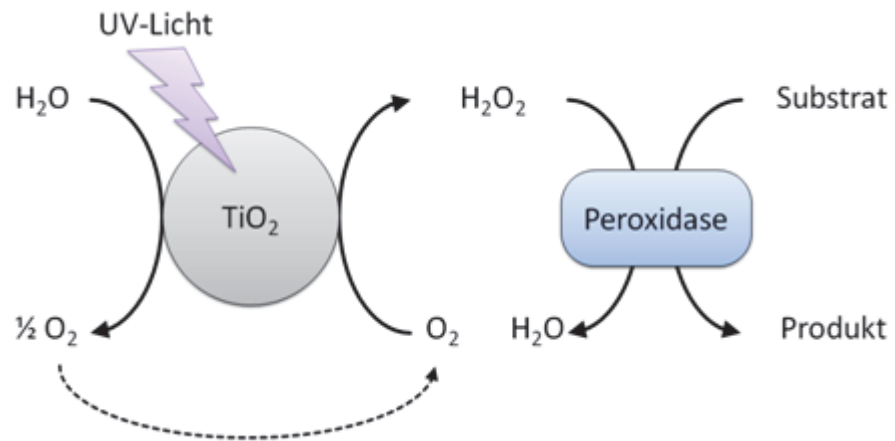
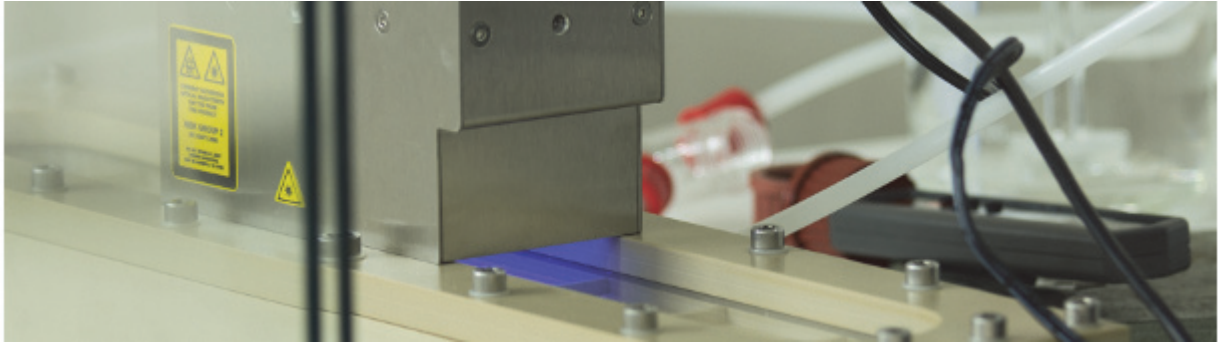


Figure 1: The combination of TiO_2 -based photocatalysis with peroxidase enzymes in a combined process for in-situ generation and utilization of H_2O_2 .

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation, BL 1425/1-1).



Improved Photocatalysts for selective NO_x-degradation



Period: 01.06.2015 - 31.08.2017

Funder: AiF

The air contamination with nitrogen oxides (NO_x) and other harmful substances such as ozone and volatile organic compounds (VOCs) presents a serious problem nowadays. The main part of these emissions is generated by anthropogenic sources, *i.e.* human activities. The European Union introduced strict maximum permissible values by the guideline 2008/50/EG to improve the air quality. Different actions taken to achieve the target values but the maximum annual average value of 40 µg/m³ NO₂ is still frequently exceeded in most German cities. The active reduction independent of the source of the amount of harmful substances by photocatalysis is a promising approach for an improved air quality. NO and NO₂ can be effectively oxidized to harmless nitrate on the surface of the photocatalyst when it is irradiated by sunlight. Afterwards, the formed nitrate will be washed off and removed by rainwater.

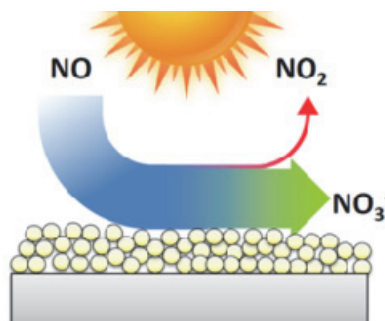


Figure 1: Scheme of the photocatalytic oxidation reaction of nitrogen monoxide over illuminated TiO₂ surfaces.

To this day, the quality of photocatalysts is only measured according to their potential to remove NO or total NO_x. There is no differentiation between the different species despite their vastly different risk potential. NO₂ is much more harmful compared to NO. If the NO₂ concentration is measured during a photocatalytic oxidation test, it becomes clear that the release of NO₂ is a critical problem. Additionally, the behavior of ozone in combination with photocatalysts is still unclear. In this project, we will explore the effect of co-catalysts on the selectivity of the reaction and the influence of ozone in the photocatalytic process will be clarified.

Supported by:



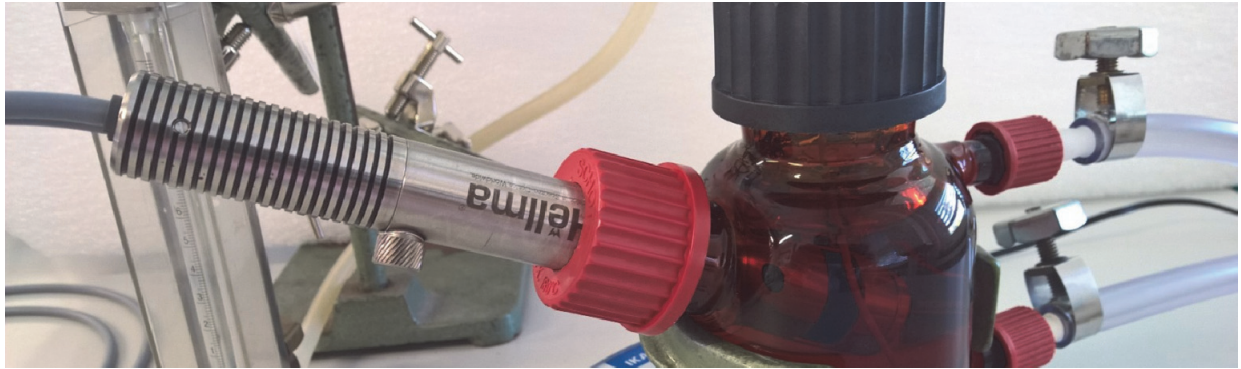
Federal Ministry
for Economic Affairs
and Energy

on the basis of a decision
by the German Bundestag

Das IGF-Vorhaben Nr. 1815210 der Forschungsvereinigung DECHEMA e.V., Theodor-Heuss-Allee 25, 60486 Frankfurt am Main wurde über die AiF im Rahmen des Programms zur Förderung der industriellen Gemeinschaftsforschung (IGF) vom Bundesministerium für Wirtschaft und Energie aufgrund eines Beschlusses des Deutschen Bundestages gefördert.



Inline quantification of NADH und NADPH under process conditions (InCo)



Period: 01.09.2014 - 31.01.2017

Funder: Deutsche Forschungsgemeinschaft (DFG)

Nicotine amide dinucleotide cofactors NADP⁺/NADPH and NAD⁺/NADH, respectively, are of paramount importance for the industrial utilization of oxidoreductases. For the rational use a knowledge gap persists between predictions based on initial rate measurements and their application in processes. The aim of the project is the inline quantification of cofactors under conditions as close as possible to process conditions by application of fluorescence spectrometry allowing monitoring at $\mu\text{mol L}^{-1}$ concentrations which are common in their application (Figure 1). The investigated enzymatic process is the enantioselective reduction of 2-octanone to (*R*)-2-octanol with LbADH with enzyme-coupled in-situ regeneration of the oxidized co-factor (NADP⁺) with GDH (Figure 2). Systematic modeling will foster the understanding of the underlying mechanisms. A generally applicable method for kinetic characterization of the reaction system will be derived. Ultimately, inline monitoring of continuous systems will be addressed. The findings expected as a result of the work are essential for the rational usage of cofactors in reductive in vitro biotransformations.

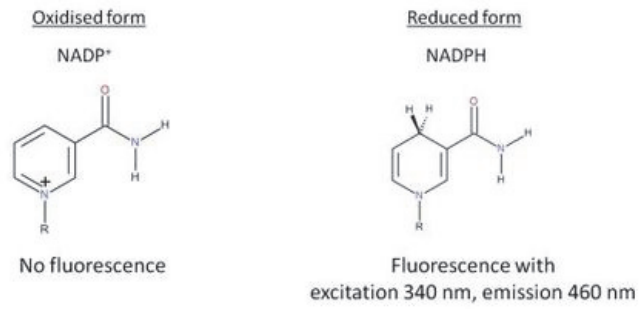


Figure 1: Different fluorescence properties of the oxidized (NADP⁺) and reduced (NADPH) forms of the cofactor

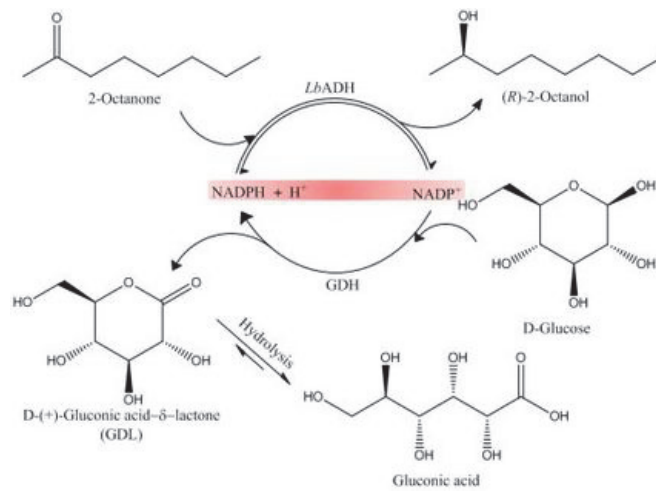
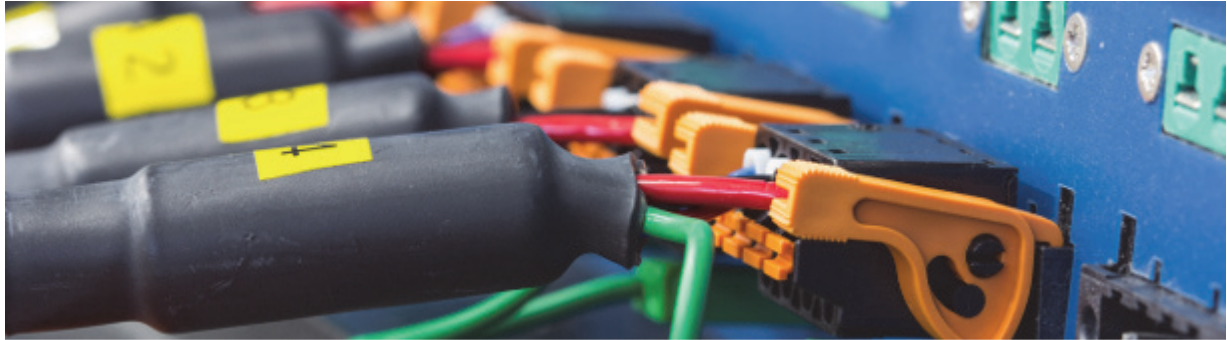


Figure 2: Reaction scheme for the enantioselective synthesis of (*R*)-2-octanol with LbADH and enzyme-coupled in-situ co-factor regeneration with GDH

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation, GR 2282/1-1)



AlSiBat - Gas diffusion electrodes for the Al-Air and Si-Air battery



Period: 01.09.2014 - 31.08.2017

Partners: TU Clausthal, TU Berlin, FZ Jülich, IoLiTec GmbH, Hoppecke GmbH, Gaskatel GmbH, Technion Israel Institute of Technology

Funder: BMBF

Motivation

According to German government strategy, contribution of renewable energy sources to electricity mix should reach 35% by 2020. In order to satisfy consumer demand, however, many challenges mostly linked to seasonal fluctuations have to be overcome. Because of their higher theoretical energy density, lower toxicity, less expensive electrode materials and non-affinity to thermal runaway in comparison with Li-based systems, metal/air batteries such as Al, Si and Zn/air are attractive candidates for sustainable energy storage applications

Background

Large scale commercialization of metal/air batteries is currently hindered by some inherent drawbacks related to the metal electrode such as poor reversibility, formation of passive layer such as $\text{Al}(\text{OH})_3$ in Al/air, shape change and dendrite formation in Zn/air as well as low energy efficiency due to high overpotentials and carbonate precipitation at the air electrode in alkaline electrolyte. In this context, recent developments in ionic liquids (IL) based aprotic electrolytes such as $\text{EMI-Cl}/\text{AlCl}_3$ open exciting perspectives especially with respect to suppression of passive layer and carbonate formation.

Most of the ILs, however, have a reduced ionic conductivity that limits current density. A typical metal/air battery design is shown in Figure 1.

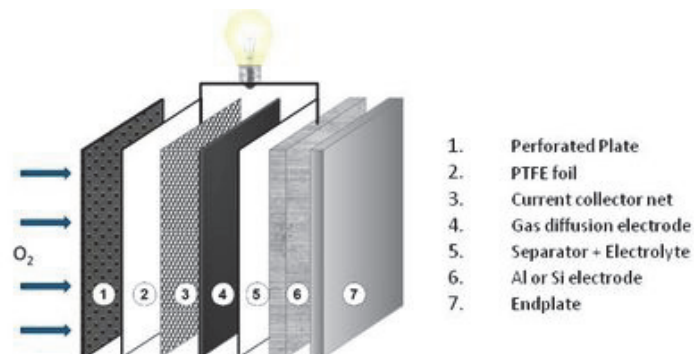


Figure1: Metal/air battery set-up

Objectives

The “AlSiBat” project aims at the development of a primary Si/air and secondary Al/air battery with appropriate IL-based electrolytes. The R&D activities of DFI in that project focus principally on the synthesis and characterization of bifunctional catalysts for oxygen reduction (ORR) during discharging and oxygen evolution (OER) during charging as well as fabrication of IL gas diffusion electrodes (GDE).

Acknowledgements

Federal Ministry of Education and Research (BMBF) is gratefully acknowledged for financial support (Förderkennzeichen: 03SFo486B)

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Allon -A Low-Cost Aluminium-Ion Battery



Period: 01.06.2015 - 31.05.2019

Partners: Acciona Infrastructure,
Accurec Recycling GmbH,
Albufera Energy Storage S.L.,
CEA - Commissariat à l'énergie atomique et aux énergies alternatives,
CEG - Elettronic Industriale S.p.a.,
Leitat Technological Center,
NTNU - Norwegian University of Science and Technology,
Solvionic,
Torrecid S.A.,
Technische Universität Berlin,
University of Southampton,
Varta Microbattery GmbH.

Funder: European commission – research and innovation program Horizon 2020

Motivation

Lithium-Ion batteries have conquered numerous market segments due to their excellent energy storage and cycling properties. Nonetheless, Li-ion technology is facing limitations with respect to overcharge, deep discharge, overheating and short-circuits that may lead to decomposition of both electrodes and electrolyte and to consecutive cell ignition (thermal runaway). Within the last decade the search for post-Li-ion batteries has been intensified. Especially the trivalent aluminum cation is an interesting candidate that possesses a remarkable theoretical capacity density of 8040 Ah L^{-1} (vs. 2046 Ah L^{-1} for Li-ion). Moreover, aluminum is abundant and cheap. However anode passivation of aluminum (Al_2O_3) in aqueous electrolytes is a major concern for reversibility. Therefore, the use of non-aqueous electrolytes with good solubility and ion conductivity for Al^{3+} should be the better strategy.

State of the Art

The best results for an Al cell so far have been published by Lin et al. who used an aluminum foil as anode, EMIMCl-AlCl₃ as electrolyte and pyrolytic graphite as cathode (see Figure 1). They presented a mechanically bendable battery that exhibited an excellent power density of 3000 W kg⁻¹, while lasting 7500 cycles without decay.^[1]

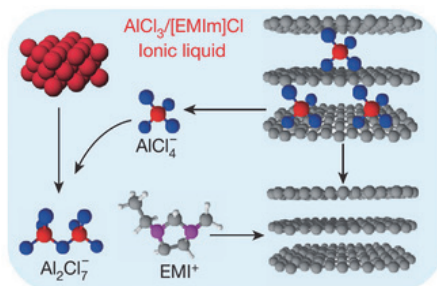


Fig. 1 - An Al-ion cell, comprising an aluminum foil anode (left), EMIMCl/AlCl₃ as electrolyte and a graphite cathode (right).^[1]

Objectives

The ALION consortium aims at the introduction of Al-ion technology into the European market by using a holistic approach. Starting with the synthesis of intercalation materials, preparation and testing of electrode materials a variety of Ionic Liquids will be screened. The determination of electrochemical data will be used for simulation and optimization of the battery at a single cell level. Al-ion cells will be manufactured and tested according to technical standards by VARTA Microbattery. The whole process will be accompanied by environmental impact evaluations as well as battery recycling considerations. DFI activities focus principally on the development and screening of intercalation materials for the anode and the cathode of Al ion batteries

For more information about project partners and objectives, please go to:

<http://www.alionproject.eu/project/>

Acknowledgements

The European Commission is gratefully acknowledged for financial support within the research and innovation program Horizon 2020. (Grant No.: 646286 – ALION)

Literature

[1] M. C. Lin et al., *Nature*, 520 (2015), 324.



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 646286.

LuZi – Bifunctional catalysts and gas diffusion electrodes for the electrical rechargeable zinc/air battery



Period: 01.07.2015 - 30.06.2018
Partner: TU Clausthal, TU Ulm, WH Gelsenkirchen, FZ Jülich,
ZSW Ulm & IoLiTec GmbH
IMRE Singapore, TU Graz, Lancaster University
Funder: BMBF

Background

Primary zinc-air batteries are widely utilized in hearing aid devices as energy supply source because of their extremely high practical capacity and energy density of about 700 mAh and 845 mWh per gram zinc, respectively.^[1] However, commercialization of rechargeable Zn/air batteries is currently hindered by some inherent drawbacks related to the metal electrode such as poor reversibility, formation of passive layer, shape change and dendrite formation as well as low energy efficiency (< 60%) due to high overpotential and carbonate precipitation at the air electrode in alkaline electrolyte. In this context, recent developments of ionic liquid (IL) based aprotic/protic electrolytes open exciting perspectives,^[2] especially with respect to suppression of dendrites, passive layer and carbonate formation. However, one of the most challenging issues is related to the air electrode reactions (ORR/OER) in ILs. A Zn/air button cell design is shown in Figure 1.

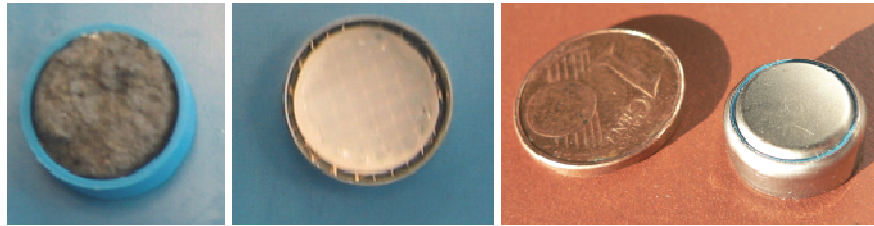


Figure 1: Zinc/air button cell with a PVA/KOH/TiO₂ membrane.^[1]

Objectives

“LuZi” project aims at the development of a secondary zinc/air battery with appropriate IL-based electrolytes. DFI activities focus on screening, development and characterization of active and stable bifunctional catalysts and gas diffusion electrodes (GDE) for the direct electric rechargeable zinc/air battery in alkaline and IL-based electrolytes.

Acknowledgements

Federal Ministry of Education and Research (BMBF) is gratefully acknowledged for financial support (Förderkennzeichen: 03SF0499B)

Literature

[1] A. Herter, V.M. Schmidt, J.-F. Drillet; Patent WO 2013 000584 A1 (2013).

[2] Y. Li, H Dai; *Chem. Soc. Rev.*, 43 (2014), 5257.

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P2X: Coking-resistant catalysts for high-temperature co-electrolysis of H₂O and CO₂ to syngas



Period: 01.09.2016 - 31.08.2019

Partners: Forschungszentrum Jülich (FZJ),
Deutsches Zentrum für Luft- und Raumfahrt (DLR),
Fraunhofer IWM/ISE, Heraeus GmbH & Co. KG,
Linde AG, Sunfire GmbH und Wuppertal Institut

Funder: BMBF

The aim of the Kopernikus project „P2X“ is to support Germany's “Energiewende” program in which energy supply from renewable sources should amount to 35% by 2020 and 80% by 2050. Especially during sunny and windy periods, excess of renewable energy production may destabilize the grid. Instead of disconnecting a certain amount of solar farms and wind mills, excess energy can be transformed meaningfully into synthesis gas, chemicals and fuels.

This ambitious challenge, however, requires innovative and flexible technological concepts that will be evaluated within the P2X project. One of these concepts aims at the development of high-temperature H₂O/CO₂ co-electrolysis to H₂/CO (synthesis gas) that serves as feedstock for production of *e.g.* methanol, gasoline and diesel via Fischer-Tropsch synthesis. The main tasks of DFI consist in developing coking-resistant catalysts for the solid-oxide electrolysis cell (SOEC) cathode and evaluating their catalytic and electrochemical activity for different H₂O:CO₂ molar ratios at 850 °C.

The influence of feed composition and reaction parameters on carbon formation will be studied as well.

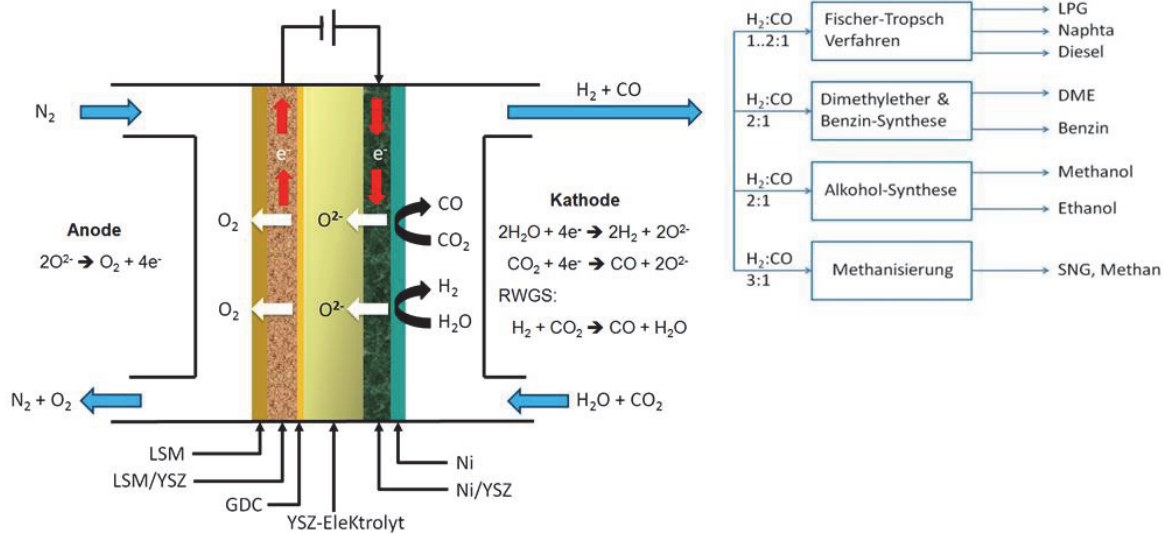


Figure 1: (Left) Principle of the H₂O/CO₂ co-electrolysis. (Right) Selection of possible end products depending on H₂:CO ratio.

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Selected publications

B. Burek, A. Sutor, D.W. Bahemann, J.Z. Bloh

Completely integrated wirelessly-powered photocatalyst-coated spheres as a novel means to perform heterogeneous photocatalytic reactions

Catalysis Science & Technology 7 (2017) 4977-4983

Heterogeneous photocatalytic reactions can be efficiently driven by completely integrated photocatalyst–light emitter units which are wirelessly powered from outside the reaction vessel using resonant inductive coupling. To demonstrate the universal applicability of the concept, three representative photocatalytic reactions, H₂O₂ production, methylene blue degradation and nitrobenzene reduction to aniline, were investigated.

J. Patzsch, J.Z. Bloh

Improved photocatalytic ozone abatement over transition metal-grafted titanium dioxide

Catalysis Today, in press (2017)

Photocatalysis can be an effective means to combat air pollution. Up to now, mainly direct NO_x abatement has been studied, but ozone abatement could also contribute significantly to improved air quality. The ozone decomposition rates of different commercial titanium dioxide based photocatalysts grafted with copper, manganese or iron ions were studied both under UVA illumination and under dark conditions. Copper and manganese grafting were effective in significantly increasing the ozone decomposition rate of the photocatalysts. The procedure worked best when using low surface area pigmentary anatase rather than nanoparticulate photocatalysts. Manganese grafting also increased the ozone abatement under dark conditions, likely due to small MnO_x clusters acting as catalysts. Iron grafting appears to be the most universal method of improving the photocatalytic ozone removal rate, as it worked for all four different photocatalysts studied. Extremely low iron grafting ratios of 0.002 at.% were sufficient to dramatically improve the performance.

J. Z. Bloh, R. Marschall

Heterogeneous Photoredox Catalysis: Reactions, Materials, and Reaction Engineering

European Journal of Organic Chemistry 15 (2017) 2085-2094

This microreview briefly summarizes recent developments in heterogeneous photoredox catalysis, with a special focus on materials, reactors, and reaction design to optimize yields. New areas such as the integration of enzymatic processes are also presented, together with an extended overview of materials, reactors, and engineering.

J. Z. Bloh

Refined Model for the Optimal Metal Content in Semiconductor Photocatalysts

Journal of Physical Chemistry C. 121 (2017) 844-851

Doping with metal ions is a simple and convenient method of improving the photocatalytic activity of semiconducting materials. As revealed previously (Bloh et al. *J. Phys. Chem. C* 2012, 116, 25558–25562), the optimal doping ratio is strongly dependent on the particle size and can be predicted with an empirical function. This work expands on that model, providing a more accurate physical explanation of the observed behavior. The new model is based on the theory that only the fraction of dopants that is situated on the particle surface has a beneficial effect. Analysis of almost 200 data points from the literature revealed that the optimal doping ratio corresponds well to an equivalent of 3.54 surface dopant atoms per particle, apparently independent of other parameters such as material or dopant. With this knowledge, the optimal doping ratio for a given catalyst can be predicted with good precision. The findings also suggest that doping and grafting essentially cause the same effect, the latter while avoiding detrimental bulk dopants. Hence, bulk doping should be avoided in favor of surface doping or grafting.

W. Zhang, B.O. Burek, E. Fernández-Fueyo, M. Alcalde, J.Z. Bloh, F. Hollmann

Selective Activation of C–H Bonds in a Cascade Process Combining Photochemistry and Biocatalysis

Angewandte Chemie International Edition, in press (2017)

Selective oxyfunctionalizations of inert C–H bonds can be achieved under mild conditions by using peroxygenases. This approach, however, suffers from the poor robustness of these enzymes in the presence of hydrogen peroxide as the stoichiometric oxidant. Herein, we demonstrate that inorganic photocatalysts such as gold–titanium dioxide efficiently provide H₂O₂ through the methanol-driven reductive activation of ambient oxygen in amounts that ensure that the enzyme remains highly active and stable. Using this approach, the stereoselective hydroxylation of ethylbenzene to (*R*)-1-phenylethanol was achieved with high enantioselectivity (>98% ee) and excellent turnover numbers for the biocatalyst (>71000).

N. Bogolowski, O. Ngaleu, M. Sakthivel, J.-F. Drillet

Long-life bifunctional BaSrCoFeO₃/C gas diffusion electrode

Carbon 119 (2017) 511-518

Several commercially available carbon black and graphitized carbon materials were first tested with respect to their thermal and electrochemical stability by thermogravimetric analysis and accelerated degradation test in 7 M KOH, respectively. KS6L and C₆₅ were the most stable systems. Because of its more than threefold higher specific volume, carbon black C₆₅ was selected as additive for gas diffusion electrode fabrication in order to increase poor electronic conductivity of as-prepared La_{0.6}Ca_{0.4}CoO₃ (LCC) and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ (BSCF) bifunctional perovskite catalysts. Especially BSCF-based gas diffusion electrode exhibited outstanding stability over 3600 h during OER/ORR cycling at 10 mA cm⁻² for 2.5 h each. This was attributed to optimal catalyst/carbon interaction and their exceptional corrosion stability in highly concentrated alkaline solution. Surprisingly, BSCF/C₆₅ showed higher activity not only for OER and but also for ORR reaction compared to that of LCC/C₆₅.

P. Ingale, M. Sakthivel, J.-F. Drillet

Test of Diethylmethylammonium Trifluoromethanesulfonate Ionic Liquid as Electrolyte in Electrically Rechargeable Zn/Air Battery

Journal of the Electrochemical Society 164 (8) (2017) H5224-H5229

A novel secondary Zn/air battery using protic Diethylmethylammonium trifluoromethanesulfonate (DEATfO) ionic liquid as electrolyte and Pt/C as gas diffusion electrode was developed. The bi-functional activity of Pt/C GDE and the quasi reversibility of Zn electro-deposition/stripping in DEATfO were demonstrated by using cyclic voltammetry method under half-cell conditions. The effect of temperature, humidity and cycling on cell performance was investigated under full-cell configuration with 0.01 M ZnTfO in DEATfO. Interestingly, in dry air and ambient air, Zn/air cell was quite stable for about 700 h. The average cell voltage of Zn || DEATfO + 0.01 M ZnTfO || Pt/C system was 1.2 and 1.8 V during discharging and charging step for 2 h each at 50 $\mu\text{A cm}^{-2}$, respectively. First experiments in ambient air were also very promising. However, maximal cell power density was relatively low (45 $\mu\text{W cm}^{-2}$). This can be explained by low contact angle of the IL on GDE substrate that presumably hindered triple-phase boundary formation.

N. Bogolowski, J.-F. Drillet

An electrically rechargeable Al-Air battery with aprotic ionic liquid electrolyte

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Some preselected aprotic ionic liquids such as EMImOTf, EMImOAc and BMPyrOTf were screened with respect to their contact angle on Pt/C and LCCO/C gas diffusion electrodes as well as their affinity to catalyze both air and aluminum reactions. Highest contact angles were measured on Pt/C GDE. While all systems showed a certain activity for ORR/ORR reactions, none of them, excepted EMImCl + AlCl₃ (1:1.5) reference electrolyte, was able to dissolve/precipitate aluminum salt on metal electrode. In that context, the Cl-based reference electrolyte was chosen for tests under full-cell conditions. Discharging/charging procedure was successfully carried out at 100 $\mu\text{A cm}^{-2}$ for 15 cycles/200 h, so that feasibility of a rechargeable Al/air cell in dried air with a aluminum foil, aprotic EMImCl + AlCl₃(1:1.5) as electrolyte and Pt/C as oxygen catalyst has been demonstrated for the first time.

N. Bogolowski, B. Iwanschitz, J.-F. Drillet

Development of a Coking-Resistant NiSn Anode for the Direct Methane SOFC

Fuel Cells 15 /5 (2015) 711-717

A coking-resistant NiSn-based membrane electrode assembly (MEA) for internal CH₄ reforming in solid oxide fuel cells (SOFCs) was developed. Catalyst powder was prepared in a centrifugal casting oven by melting stoichiometric amounts of Ni and Sn under vacuum. The formation of Ni₃Sn₂ intermetallic phase was confirmed by XRD analysis. Catalytic activity for CH₄ reforming and stability of the NiSn powder were first evaluated in a quartz glass reactor for 4 h at 600–1,000 °C. The main reaction products H₂ and CO were detected by gas chromatography while no carbon formation was detected during the experiments. Then, 3YSZ electrolyte-supported MEAs were fabricated with a Ni₃Sn₂/YSZ anode and LSM/YSZ cathode and characterized under SOFC conditions. The MEA showed an excellent stability under CH₄ atmosphere (3% H₂O) at 850 °C over more than 650 h. No substantial decrease in cell potential was observed during this period.

M. Sakthivel, I. Radev, V. Peinecke, J.-F. Drillet

Highly Active and Stable Pt₃Cr/C Alloy Catalyst in H₂-PEMFC

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The as-prepared 40 wt% Pt₃Cr/C alloy catalyst showed enhanced activity under both half-cell and full-cell conditions as well as excellent corrosion stability compared to those of the 40 wt% Pt/C benchmark catalyst. In half-cell experiments at 2 mA cm⁻², Pt₃Cr/C catalyst exhibited 10 mV less over-potential and twofold higher specific and mass activity for ORR than Pt/C. The average particle size grew from 4.5 nm up to “only” 6–8 nm after 7000 degradation cycles. For comparison, average particle size of Pt/C increased from 4.5 up to 10–30 nm. After 1000 degradation cycles in full-cell, MEA with Pt₃Cr/C cathode exhibits an excellent maximum power density retention of about 94% compared to only 59% for the MEA with the commercial catalyst.

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Contact:

Dr. Jonathan Z. Bloh
Head of Chemical Technology
+49 69 7564 387 – bloh@dechema.de

Dr. Jean-Francois Drillet
Senior Scientist Batteries and Fuel Cells
+49 69 7564 476 – drillet@dechema.de

DFI Secretariat
+49 69 7564 252 or 337 - dfi@dechema.de

DECHEMA-Forschungsinstitut

Theodor-Heuss-Allee 25
60486 Frankfurt am Main