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# Electrochemical Carbon Dioxide Reduction to Formic Acid in a Flow Cell using Molecular Catalysts

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**ENERGIE & NACHHALTIGKEIT**  
Nachhaltige CO<sub>2</sub>-Kreisläufe

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using Molecular Catalysts**

Elektrische  
Energiespeichersysteme



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Elektromobilität &  
Batterietechnologie



Cuvillier Verlag Göttingen  
Internationaler wissenschaftlicher Fachverlag

<https://cuvillier.de/de/shop/publications/8752>

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# 1 | Abstract

This work addresses the gap between basic research and applied research in the field of CO<sub>2</sub> electrolysis using molecular catalysts. The development of new catalysts should include important aspects of the industrial application as early as possible to unlock the true potential of a catalyst and also to prevent potential problems that occur when changing to industrially relevant process conditions.

The development of new energy solutions and alternative non-fossil carbon sources is a major challenge for the next decades. The success of these efforts will impact the live of every person, probably not today or tomorrow but certainly at a point in the future. History shows that a new technology needs between 10 to 15 years of research and development before it is applicable on a large scale. At the same time the issues of energy supply and alternative carbon sources are not short lived and will get more pressing in the future. Therefore it is necessary to investigate new ways today in order to have working and scalable technologies in 10 years time.

In a first step the present thesis investigates a non-electrochemical reaction, the transfer hydrogenation (TFH), in a pressurized autoclave setup. The TFH of CO<sub>2</sub> with isopropanol (iPrOH) as hydrogen donor was successful and turnover number (TON) of around 20 are in the same range as the only literature reported TFH with CO<sub>2</sub> as substrate<sup>[1-3]</sup>. The transfer to an electrochemical reaction control proved that electrochemical catalysis requires specific catalysts as the transfer of the TFH catalyst was not straight forward. The issue was addressed by establishing a cyclic voltammetry (CV) based approach to asses potential catalysts. In order to test these catalysts with respect to activity, selectivity and stability a proto-

type flow cell was developed that allowed electrolysis under exclusion of air and in organic solvent under flow conditions. Hence, several alternative catalysts were tested *via* CV, leading to  $\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene ( $\text{CpFe}(\text{dppf})(\text{CO})$ ),  $\text{Cu-Si-MACHO}^{\text{Ph}}$ , cobaltocene and chlorotricarbonyl(2,2'-bipyridine)rhenium(I) ( $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ ) as candidates for further investigation in the developed prototype flow cell.

Cobaltocene and  $\text{CpFe}(\text{dppf})(\text{CO})$  predominantly produced the undesired hydrogen as product, which is, in case of the latter, explained by the Fe metal center, which could be exchanged by other metals to access a different product spectrum.  $\text{Cu-Si-MACHO}^{\text{Ph}}$  gave 60 % formate showed very promising results, however, copper precipitates on the cathode suggest an insufficient stability under reduction conditions.  $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$  was intended as a benchmark compound but surprisingly displayed a selectivity towards formate that is not reported in literature. The hypothesis of a reaction engineering effect as cause for the change in selectivity was disproved experimentally, identifying the cathode material as the only difference with respect to the literature. Literature focused on catalyst development is conducted using glassy carbon electrodes, in the present thesis graphite was used as it is the standard material in flow cell applications. Physical and chemical analyses of the cathode material suggest a interaction between the graphene sheets within the graphite electrode that alters the electron configuration of the complex to favour hydride formation, which is the intermediate step towards formate.

The results show that unexpected phenomena can occur when scaling up a technology from lab scale to pilot, or even industrial scale, advocating to make an effort to come as close as possible to large scale conditions, already in the lab. That can prevent major setbacks in the process and save valuable time and effort. This aspect is underlined by recent research in the specific field of  $\text{CO}_2$  electrolysis using organometallic complexes, as catalysts show different performance characteristics after immobilization, for example. The successful development of future solutions depends on the interdisciplinary collaboration that takes into account molecular considerations as well as process engineering aspects.

## 2 | Zusammenfassung

Diese Arbeit adressiert die Lücke zwischen der Grundlagenforschung und der angewandten Forschung auf dem Gebiet der molekular katalysierten co-Elektrolyse. Bei der Entwicklung neuer Katalysatoren sollten wichtige Aspekte der industriellen Anwendung so früh wie möglich einbezogen werden, um das wahre Potenzial eines Katalysators zu erschließen und auch um mögliche Probleme zu vermeiden, die beim Wechsel zu industriell relevanten Prozessbedingungen auftreten können.

Die Entwicklung neuer Energielösungen und nicht-fossiler Kohlenstoffquellen ist eine der größten Herausforderungen der nächsten Jahrzehnte. Der Erfolg dieser Bemühungen wird sich auf das Leben eines jeden Menschen auswirken, wahrscheinlich nicht heute oder morgen, aber sicherlich irgendwann in den kommenden Jahrzehnten. Erfahrungswerte zeigen, dass eine neue Technologie zwischen 10 und 15 Jahren Forschung und Entwicklung benötigt, bevor sie in großem Maßstab anwendbar ist. Die Fragen der Energieversorgung und alternativer Kohlenstoffquellen sind nicht kurzlebig und werden in Zukunft noch drängender werden. Deshalb ist es notwendig, heute neue Wege zu erforschen, um in 10 Jahren über funktionierende Technologien zu verfügen.

In einem ersten Schritt der vorliegenden Arbeit wurde eine nicht-elektrochemische Reaktion, die Transferhydrierung, in einem unter Druck stehenden Autoklaven untersucht. Die Transferhydrierung von  $\text{CO}_2$  mit Isopropanol (iPrOH) als Wasserstoffdonor war erfolgreich und die ermittelte turnover number (TON) von etwa 20 liegt im gleichen Bereich der einzigen literaturbekannten Transferhydrierung mit  $\text{CO}_2$  als Substrat<sup>[1-3]</sup>. Die Übertragung auf eine elektrochemische Reaktionskontrolle zeigte, dass die elektrochemische Katalyse

spezifische Katalysatoren erfordert, da der Transferhydrolyse-Katalysator nicht ohne Weiteres in der Elektrolyse eingesetzt werden konnte. Das Problem wurde durch die Einführung eines auf Cyclovoltammetrie (CV) basierenden Ansatzes zur Bewertung potenzieller Katalysatoren angegangen. Um diese Katalysatoren im Hinblick auf Aktivität, Selektivität und Stabilität zu testen, wurde ein Prototyp einer Durchflusszelle entwickelt, der die Elektrolyse unter Luftausschluss und in einem organischen Lösungsmittel unter Durchflussbedingungen ermöglicht. Daher wurden mehrere alternative Katalysatoren mittels Cyclovoltammetrie getestet, wobei  $\text{CpFe(dppf)(CO)}$ ,  $\text{Cu-Si-MACHO}^{Ph}$ , Cobaltocen und  $\text{Re(bpy)(CO)}_3\text{Cl}$  als Kandidaten für weitere Untersuchungen in der entwickelten Durchflusszelle ausgewählt wurden. Cobaltocen und  $\text{CpFe(dppf)(CO)}$  produzierten überwiegend den unerwünschten Wasserstoff als Produkt, was im letzteren Falle durch das Fe-Metallzentrum erklärt wird, das durch andere Metalle ausgetauscht werden könnte, um ein anderes Produktspektrum zu erhalten.  $\text{Cu-Si-MACHO}^{Ph}$  lieferte 60 % Formiat, was sehr vielversprechend war, wären da nicht die Kupferausfällungen auf der Kathode, die auf eine unzureichende Stabilität unter Reduktionsbedingungen schließen lassen.  $\text{Re(bpy)(CO)}_3\text{Cl}$  war als Benchmark-Katalysator gedacht, überraschte aber mit einer Selektivität zu Formiat, welche in der Literatur nicht beschrieben ist. Die Hypothese eines reaktionstechnischen Effekts als Erklärung für die Formiatbildung wurde experimentell widerlegt. Das bedeutet, dass das Kathodenmaterial den einzigen Unterschied zur Literatur darstellt und somit die Formiatbildung verursachen muss. In der Literatur zur Katalysatorentwicklung werden Elektroden aus Glassy Carbon verwendet. In der vorliegenden Arbeit wurde Graphit verwendet, da es das Standardmaterial für Durchflusszellenanwendungen ist. Die physikalische und chemische Analyse des Kathodenmaterials deutet auf eine starke Wechselwirkung zwischen den Graphenschichten innerhalb der Graphitelektrode hin, die die Elektronenkonfiguration des Komplexes so verändert, dass die Bildung der Hydridspezies begünstigt wird, welches ein Intermediat der Formiatbildung darstellt.

Die vorgestellte Arbeit konzentriert sich auf die Lücke zwischen Grundlagenforschung und angewandter Forschung und weist darauf hin, wie wichtig es ist Anwendungsaspekte

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bereits in sehr frühen Stadien der Katalysatorentwicklung zu berücksichtigen. Die Ergebnisse zeigen, dass unerwartete Einflüsse auftreten können, wenn eine Technologie vom Labormaßstab in den Pilot- oder industriellen Maßstab überführt wird. Dies kann größere Rückschläge im Prozess verhindern und wertvolle Zeit und Mühe sparen. Auf dem speziellen Gebiet der molekular katalysierten co-Elektrolyse weisen aktuelle Veröffentlichungen anderer Arbeitsgruppen in dieselbe Richtung, wenn Katalysatoren beispielsweise nach der Immobilisierung veränderte Leistungsmerkmale aufweisen. Die erfolgreiche Entwicklung künftiger Lösungen hängt von der interdisziplinären Zusammenarbeit ab, bei der sowohl molekulare als auch verfahrenstechnische Aspekte berücksichtigt werden.



## 3 | Introduction

”It is unequivocal that human influence has warmed the atmosphere, ocean and land. Widespread and rapid changes in the atmosphere, ocean, cryosphere and biosphere have occurred.”<sup>[4]</sup>

— 2021 Report of the Intergovernmental Panel on Climate Change (IPCC) —

This clear statement originates from the recent report on climate change published by the Intergovernmental Panel on Climate Change (IPCC) and hence reflects the scientific assessment of the vast majority of world leading scientists. The origin of the climate crisis can be clearly linked to human actions of which CO<sub>2</sub> emissions from fossil fuel combustion are the main driver. To counteract the effects described by the IPCC, drastic reductions in greenhouse gas (GHG) emissions are required across all sectors. The IPCC and researcher around the world calculate which effects will occur for different scenarios of continued emission. And political decision makers start to commit to the targets (Paris Agreement), details on the scenarios are beyond the scope of this work (the interested reader is kindly referred to the literature<sup>[5-9]</sup>) but it is very clear that a significant challenge is ahead of the human kind and no opportunity to act should be left aside. The prevention of catastrophic consequences can not be achieved by technological solutions alone. An increased efficiency will not prevent an increase of global emissions as it is by far outweighed by a growing population and globally growing economies that are bound to produce CO<sub>2</sub> emissions in ever increasing quantities. Changes have to be pursued on all levels of our society, on how politics is shaping our society, the way that the world economy works, the definition of wealth, questions of global justice, international cooperation with respect to global questions, how we prepare for the inevitable climatic changes to come and how we prepare and educate our future generations to cope with a changing world. Much hope was laid on the decoupling of emissions from economic growth. Amongst the hopeful was Barack Obama in his text ” The irreversible momentum of clean energy”<sup>[10]</sup>, but the statistics are unambiguous and a complete decoupling is far from trivial<sup>[11]</sup>. The continued growth of the world economy is incompatible with the climate targets. Research is also conducted in these areas attempting to outline possible alternative economic models, like degrowth<sup>[12]</sup> and ways to live in accordance to



the climate targets. Although this is not a new idea and the Club of Rome warned as early as 1972 that limitless growth is not possible on a limited planet<sup>[13]</sup>, very little progress has been made on the matter.

Electrolysis is regarded as one key technology of the future as it makes use of renewable electricity to convert substances either as energy storage vector or to produce chemicals, thus replacing fossil based and fossil driven processes<sup>[14]</sup>. The electrification of the production as well as the mobility and heating sector are the next steps to take, as it is comparatively easy to change these processes on a large scale, thus creating the biggest impact on the climate goals. Water electrolysis is a famous example as there are large electrolyzers in the 20 MW range commercially available<sup>[15;16]</sup>. However, in the mid-term more challenging sectors, such as steel production, cement production and the chemical sector have to decrease CO<sub>2</sub> emissions and new solutions must be researched today in order to be available in time to reach the emission targets.

In this thesis the special case of CO<sub>2</sub> electrolysis is investigated, which has the potential to mitigate CO<sub>2</sub> emissions, as waste streams can be used as substrate (*e.g.* from cement or steel plants) and replace fossil based chemicals thus contributing to the emission reduction on multiple levels. Siemens Energy and Evonik recently built the first demonstration plant with a electrolyzer capacity of 25 kW producing syngas (CO and H<sub>2</sub>) which is subsequently fermented to fine chemicals like hexanol and butanol, which can be used in cosmetics<sup>[17]</sup>. This example shows that CO<sub>2</sub> electrolysis is not yet a turnkey process, but the potential to contribute to future challenges cannot be underestimated and an increasing attention of businesses and society is boosting the scientific effort which started many years ago<sup>[18–22]</sup>.

The research on this topic reaches from catalyst development, to reactor design and system integration. The presented thesis aims towards the establishment of a concerted catalyst development procedure. The idea is that catalyst development can be more targeted and efficient if process conditions, like electrode architecture and flow regime, are already included in early stage research, as was recently nicely described by SIEGMUND *et al.*<sup>[23]</sup>. However, such a flow cell system that allows the assessment of activity, selectivity and stability of molecular catalysts does not exist at the start of the presented research. This thesis focusses on the testing and developing of next generation catalysts for CO<sub>2</sub> electrolyzers based on organometallic complexes.

## 4 | Carbon Dioxide Reduction to Formic Acid using Molecular Catalysts

The activation of the stable molecule carbon dioxide ( $\text{CO}_2$ ) requires catalysts that are highly active so the reaction barriers are overcome. Once activated  $\text{CO}_2$  can be converted to a number of products, from C1 species like carbon monoxide, formaldehyde, formic acid (or formate) to C2 and C3 species. Therefore a suitable catalyst also needs to achieve a certain selectivity in order to accommodate a reasonable  $\text{CO}_2$  conversion process. Available catalyst systems are divided into two main categories: molecular catalysts and solid catalysts. Generally solid catalysts tend to be more robust and practical in application as they are in a different phase as the reactants and can therefore be easily separated after the reaction. However, mechanistic conclusions are difficult to draw as the active center is not exactly defined. The defined active center is the advantage of molecular catalysts, which can be tailored by choosing the metal center and adapting the ligand structure. However, molecular catalysts are more sensitive to deactivation by impurities like air or water and mostly they are applied homogeneously in the same phase as the reactants, which necessitates a separation step in the process<sup>[24;25]</sup>. The gap between these catalyst systems has become smaller over the past years as intense research is focussed at facilitating the best of the two worlds in one system<sup>[26–30]</sup>. This can be approached by immobilizing a molecular catalyst on a surface, or by reducing the particle size of the heterogeneous catalysts by advanced synthesis methods in a way that leads to single atom catalysts (SACs) that are as defined as molecular catalysts<sup>[31–33]</sup>.

With this vast research field in mind it is necessary to focus the following assessment of the state of the art. The research question addresses the potential of molecular catalysts and this is also the focus of the literature research conducted with occasional excursion to adjacent topics like the immobilization of molecular catalysts on the surface of a support.

## 4.1 Direct Carbon Dioxide Reduction to Formic Acid with Molecular Catalysts and Hydrogen as Reactant

In the following subsections systems are reviewed that use organometallic catalysts to reduce CO<sub>2</sub> in the presence of molecular hydrogen. In subsection (4.1.1) organometallic catalysts are discussed together with their specific requirements regarding reaction conditions as well as principal mode of operation of the catalysts. Subsection (4.1.2) deals with switchable systems that accommodate the reduction of CO<sub>2</sub> to value added products as well as the reverse reaction, thus providing interesting hydrogen storage capabilities requiring only a single catalytic system.

### 4.1.1 Organometallic Catalysts

The hydrogenation of CO<sub>2</sub> using molecular catalysts is a well understood process and investigations regarding the effect of catalysts, solvents, additives and reaction conditions are numerous<sup>[34–47]</sup>. They are well represented by a review of COKOJA *et al.*<sup>[48]</sup> and more recently by SORDAKIS *et al.*<sup>[49]</sup> who also includes dehydrogenation considerations for potential energy storage applications. Concluding these investigations advantageous systems are Ru-, Rh- or Ir- complexes with ligands that are well suited to stabilize the intermediates. The solvent has to be chosen according to the ligand-type and the desired product. The range of possible solvents includes water, ethanol, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), acetonitrile and many more. In general it is suggested to choose a polar organic solvent, since organic solvents dissolve more CO<sub>2</sub><sup>[50;51]</sup>, hence the substrate availability is influenced, which can be a rate limiting factor. Furthermore OHNISHI *et al.*<sup>[52]</sup> found in a theoretical calculation polar solvents to be more suited because they accelerate the rate limiting step of CO<sub>2</sub> insertion into the M-H bond. BELLER *et al.*<sup>[53]</sup> supports this as they point out that the hydrogenation of CO<sub>2</sub> is energetically unfavored ( $\Delta G^\circ = 32.9 \text{ kJ mol}^{-1}$ ) due to the high entropic contribution and by using polar solvents like H<sub>2</sub>O or DMF and alcohols or amines as additives formic acid can be stabilized causing the process to become exergonic ( $\Delta G^\circ = -4 \text{ kJ mol}^{-1}$  in case of water as solvent).

INOUE *et al.*<sup>[54]</sup> reported the first molecular hydrogenation of CO<sub>2</sub> to HCOOH using group VIII transition metal complexes in 1976 testing different complexes with amines (bases) and water as co-catalysts, as small amounts of those accelerated the reaction. The best catalyst reported by INOUE *et al.*<sup>[54]</sup> is the H<sub>2</sub>Ru(PPh<sub>3</sub>)<sub>4</sub>. The amine with the best results, diazabicyclo[5.4.0]undec-7-ene (DBU), is similar to the amine used by HSU *et al.*<sup>[55]</sup> who published promising results on the reversible formation of a DBU-formate adduct.

A similar catalyst to the one used by HSU *et al.*<sup>[55]</sup> was tested by KOTHANDARAMAN *et al.*<sup>[56]</sup>