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# 8

## **Summary, conclusions and future prospects**

## 8.1 Summary

Carbon dioxide plays a vital role in life as we know it, since it is the primary source of carbon in life on Earth. Ever since the Industrial Revolution, between 1760-1840, the concentration of carbon dioxide in the atmosphere has been rising rapidly due to increasing man-made carbon dioxide emissions. These emissions are primarily due to the increasing consumption of fossil fuels. Since the rise in carbon dioxide concentrations in the atmosphere could have serious consequences for the biosphere and the conditions on Earth, there is a need to control the amount of carbon dioxide in the atmosphere and to control our carbon dioxide emissions.

The research described in this thesis deals with the electrocatalytic reduction of carbon dioxide to fuels and useful chemicals on nanostructured electrocatalysts. Electrocatalytic carbon dioxide reduction can possibly be used to control the amount of carbon dioxide in the atmosphere and to close the anthropogenic carbon cycle. If renewable energy is used for the reduction of carbon dioxide, this system can also be used as a means to store renewable energy. Important parameters in designing and testing new electrocatalysts for the reduction of carbon dioxide are the overpotential necessary to reduce  $\text{CO}_2$ , as it is a measure of the energy efficiency of the catalysts, and the current density, which is a measure for the rate of the electrocatalytic reaction. Furthermore, the product distribution during  $\text{CO}_2$  reduction is studied via online methods such as OLEMS, online HPLC and GC.

First an overview of reported heterogeneous and immobilized homogeneous electrocatalysts for the reduction of  $\text{CO}_2$  and the pathways via which they form products is given in Chapter 2. Substantial effort has been invested in understanding the mechanism of  $\text{CO}_2$  reduction on copper, since copper has unique catalytic abilities and is the only catalyst that is able to produce hydrocarbons such as methane, ethane and ethanol with decent faradaic efficiencies. The mechanism of  $\text{CO}_2$  reduction on other metals remains largely unclear. We also note that the parameters such as the electrolyte composition and pH can change the outcome of the reaction drastically.

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In Chapter 3 the electrocatalytic reduction of CO<sub>2</sub> on copper electrodes in weakly alkaline media is discussed. Since a carbonate buffer is created when an alkaline solution is purged with CO<sub>2</sub>, this system has not been studied before. We observe a difference in the voltammetry of CO<sub>2</sub> reduction in phosphate buffer electrolytes with different initial pH values. In an electrolyte that had an initial pH of 11.6, a reduction peak was seen around -0.6 – -0.7 V vs. RHE. This reduction peak had been observed before in the literature and was ascribed to the formation of a layer of adsorbed CO, which is an intermediate in CO<sub>2</sub> reduction on copper. However, with the aid of online HPLC we show that formic acid is produced at the potentials where the reduction peak is seen in the voltammetry. Furthermore, we show that formic acid is also produced at these potentials in a bicarbonate buffer in the absence of CO<sub>2</sub>. Therefore, we postulate that the observed reduction peak is due to either direct or indirect bicarbonate reduction on copper. The reduction of bicarbonate on copper is influenced by the anionic and cationic species that are present in the electrolyte and can be boosted by roughening the electrode.

For two-electron transfer reaction “reversible electrocatalysts” are expected to exist, since typically only a single intermediate needs to be stabilized. Therefore, we have studied the ability of an active formic acid oxidation catalyst to perform the reverse reduction of CO<sub>2</sub> to formic acid in Chapter 3. Since active formic acid oxidation catalysts generally consist of either platinum or palladium, we have combined both platinum and palladium in an effort to create an electrocatalyst that is able to perform reversible catalysis. The onset potential of CO<sub>2</sub> reduction to formic acid on electrodeposited palladium layers on a polycrystalline platinum electrode was -0.05 V vs. RHE, a shift in onset potential of more than 1 V compared to a polycrystalline palladium electrode. Moreover, this onset potential is very close to the theoretical equilibrium potential of 0.02 V vs. RHE in this electrolyte. At low overpotentials a peak in the production of formic acid was observed, while at higher overpotentials a continuous production of formic acid was seen. The low overpotential production peak was linked to the either direct or indirect reduction of bicarbonate, while the high overpotential production was due to direct CO<sub>2</sub> reduction. Finally, we showed that reversible reduction of CO<sub>2</sub> to formic acid and formic acid oxidation to CO<sub>2</sub> can take place on

the Pd-Pt electrode. The production of formic acid from  $\text{CO}_2$  is however hindered by a deactivation of the catalyst that is probably caused by CO poisoning.

In an effort to overcome this deactivation, and to thus create an active catalyst for  $\text{CO}_2$  reduction to formic acid, a series of  $\text{Pd}_x\text{Pt}_{(100-x)}/\text{C}$  nanoparticles were synthesized and tested for their catalytic properties in Chapter 5. We show that the optimal composition for formic acid oxidation is  $\text{Pd}_{90}\text{Pt}_{10}/\text{C}$ . This is explained by the breaking up of platinum ensembles that are active for the dehydration of formic acid to CO and therefore responsible for CO poisoning of the catalyst. The optimal composition for  $\text{CO}_2$  reduction to formic acid is  $\text{Pd}_{70}\text{Pt}_{30}/\text{C}$ , indicating that the breaking up of platinum ensembles is less important for  $\text{CO}_2$  reduction than for formic acid oxidation. The superior catalytic properties of  $\text{Pd}_{70}\text{Pt}_{30}/\text{C}$  are ascribed to the fine tuning of the d-band center by mixing Pd and Pt and the lattice strain that can be induced by the addition of the bigger platinum atoms. A maximum faradaic efficiency toward formic acid of 88% is achieved after one hour of electrolysis at -0.4 V vs. RHE, proving that the fast deactivation that was seen previously with the Pd-Pt electrodes can be overcome by tuning the composition of the catalyst. This faradaic efficiency is higher or competitive with efficiencies reported for other catalysts, but was achieved at substantially lower overpotentials. Unfortunately, there was still a decrease in faradaic efficiency to 58% after two hours of electrolysis.

In Chapter 6 the electrochemical reduction of  $\text{CO}_2$  on PdAu electrodes is studied. The combination of palladium and gold was chosen in order to tune the binding strength of CO on the surface of the catalyst, since it has been proposed in the literature that this is a key parameter in designing an electrocatalyst that is able to reduce  $\text{CO}_2$  to hydrocarbons. Both with electrodeposited layers of palladium on a polycrystalline gold electrode and with monolayers of palladium on a polycrystalline gold electrode we observe the formation of  $\text{C}_1\text{-C}_5$  hydrocarbons, consisting of methane, ethylene, ethane, propylene, propane, 1-butene, isobutane, butane, 2-methyl-butane, pentane and pentene, albeit with low faradaic efficiencies. Besides these gaseous products, soluble products such as formic acid, methanol, ethanol and acetic acid are observed. We propose that the higher hydrocarbons products are formed via the polymerization of  $-\text{CH}_2$  intermediates adsorbed on the surface of the catalyst. By increasing the amount

of palladium on a polycrystalline gold electrode we show that the activity toward the production of higher hydrocarbons increases, therefore indicating that the active catalyst is most likely a palladium rich PdAu alloy near or on the surface.

The effect of the support material during the reduction of CO<sub>2</sub> and oxidation of formic acid on Pd<sub>70</sub>Pt<sub>30</sub> nanoparticles, that were developed in Chapter 5, is studied in Chapter 7. A clear support effect is observed for both formic acid oxidation and CO<sub>2</sub> reduction. The electro-oxidation of formic acid shows higher current densities in the forward scans on reduced graphene (rGO) and multi-walled carbon nanotubes (MWCNT) supported nanoparticles. In the backward scan the MWCNT supported nanoparticles display far superior current densities to both the rGO and Vulcan XC-72 supported nanoparticles. The reduction of CO<sub>2</sub> toward formic acid on rGO supported nanoparticles shows poor faradaic efficiencies at all studied potentials. A peak in faradaic efficiency toward formic acid is seen at -0.2 V vs. RHE for MWCNT supported nanoparticles, while the faradaic efficiency toward formic acid production on Vulcan XC-72 peaks at -0.4 V vs. RHE, as was shown before. The faradaic efficiency of CO<sub>2</sub> reduction toward formic acid is close to 100% at the MWCNT supported nanoparticles after 30 minutes of electrolysis and decreases to 64% after two hours of electrolysis.

## 8.2 General conclusions

The aim of the research described in this thesis was to develop and study selective and efficient nanostructured electrocatalysts for the reduction of CO<sub>2</sub> to valuable products. We have shown that for 2-electron transfer products, such as formic acid, it is possible to design a selective catalyst via the concept of reversible catalysis. This palladium and platinum based catalyst is able to perform both formic acid oxidation to CO<sub>2</sub> and CO<sub>2</sub> reduction to formic acid, showing for the first time that reversible CO<sub>2</sub> reduction can take place on a heterogeneous electrocatalyst.

By tuning the composition of Pd<sub>x</sub>Pt<sub>(100-x)</sub>/C nanoparticles fast deactivation was overcome and an optimal faradaic efficiency of 88% after 1 hour of

electrolysis at -0.4 V vs. RHE was achieved. Furthermore, we have shown that the support material has a significant effect on the catalytic properties of the nanoparticles.

A study of CO<sub>2</sub> reduction in weakly alkaline media on copper electrodes revealed that bicarbonate can be reduced, either by direct or indirect reduction, to formic acid. Since this had never been observed before and the reduction peak in the voltammetry that was linked to formic acid production was ascribed to the formation of a CO ad-layer on the catalyst surface in previous studies in the literature, this study has provided new mechanistic insight into the reduction of CO<sub>2</sub> on copper.

Finally, a electrocatalyst for the reduction of CO<sub>2</sub> to C<sub>1</sub>-C<sub>5</sub> hydrocarbons was developed. This was done by combining a metal which bind CO too strongly, palladium, with a metal which binds CO too weakly, gold, in an effort to tune the binding strength of CO on the surface of the catalyst. This catalyst is unique, since it is to the best of our knowledge the first non-copper-containing catalyst that produces a variety of multi-carbon products.

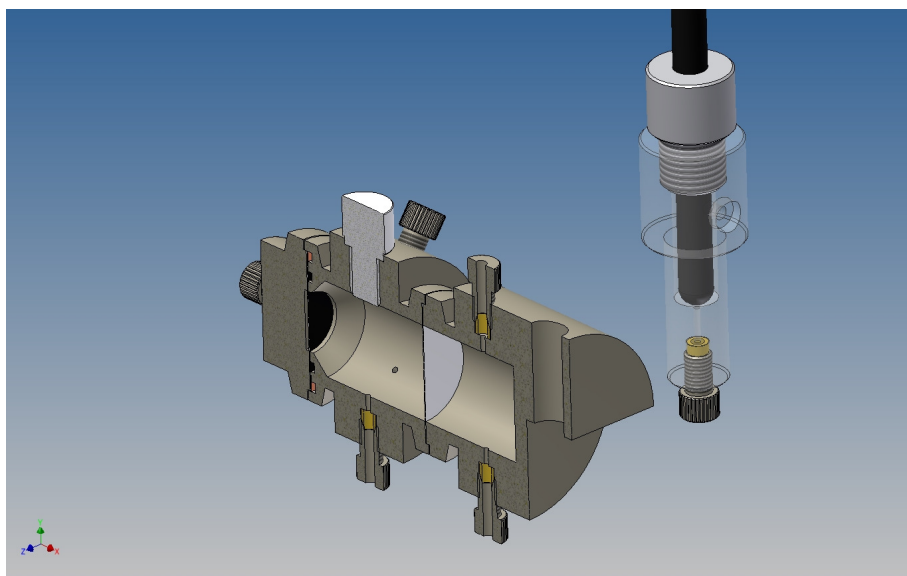
### 8.3 Future prospects

This thesis has proven that bimetallic electrocatalysts can be designed and optimized to produce valuable products from CO<sub>2</sub>. In future research, inspiration can be taken from for example biological system and theoretical research. To break the universal scaling relationships that exist for the reduction of CO<sub>2</sub> and cause intrinsic overpotentials, catalysts with multiple binding modes need to be developed. Also here bimetallic electrocatalysts can be of added value.

To further explore the possibilities of the Pd<sub>70</sub>Pt<sub>30</sub> nanoparticles on different supports that have been developed in Chapter 5 and 7, they can be employed in a gas diffusion electrode setup. Gas diffusion electrodes can overcome mass transport limitations that are present at solid electrodes, thereby increasing the maximum reaction rates, measured as current densities. This is an important parameter since this will determine the reactor size and thus the

capital costs of the process. Moreover, due to the small distance that dissolved  $\text{CO}_2$  has to travel to reach the catalyst, the local  $\text{CO}_2$  concentration near the electrode can be significantly increased in comparison to a solid electrode in an aqueous electrolyte. This increase in  $\text{CO}_2$  concentration can be beneficial to both the reaction rate and the faradaic efficiency of  $\text{CO}_2$  conversion to formic acid, since an increase in the amount of  $\text{CO}_2$  near the electrode could further decrease the rate of hydrogen evolution. To study the electrochemical reduction of  $\text{CO}_2$  to formic acid on  $\text{Pd}_x\text{Pt}_{(100-x)}$  nanoparticles in a gas diffusion electrode setup, a new cell has already been developed (see Figure 8.1).

Next to that, we plan to study morphology changes of the  $\text{Pd}_{70}\text{Pt}_{30}$  nanoparticles after electrolysis with Identical Location Transmission Electron Microscopy (IL-TEM). By identifying these morphology changes, further light can be shed on the deactivation pathways that are responsible for the decrease in faradaic efficiency toward formic acid on  $\text{Pd}_{70}\text{Pt}_{30}$  that is observed at longer electrolysis times.



**Figure 8.1** Schematic cut through drawing of the employed PEEK cell for experiments with gas diffusion electrodes. The cell consists of an anode and cathode compartment separated by a Nafion 115 membrane and a reference compartment that was connected with Teflon tubing to the cathode compartment.

