Temperature and pressure effects on the electrochemical CO2 reduction

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Outlook

This thesis has mainly discussed the effect of temperature on the electrochemical CO_2 reduction. It has also shown the important effect of pressure with the newly developed high-pressure high-temperature electrochemical cell. However, this cell was only completed near the end of my PhD. Therefore, this work is only the start of the understanding of the effect of temperature and many more studies are possible in this unique setup. The next section presents suggestions for future studies as well as some insights that I gained during my PhD, but could not complete into a chapter of this thesis.

O.1 Cu instability

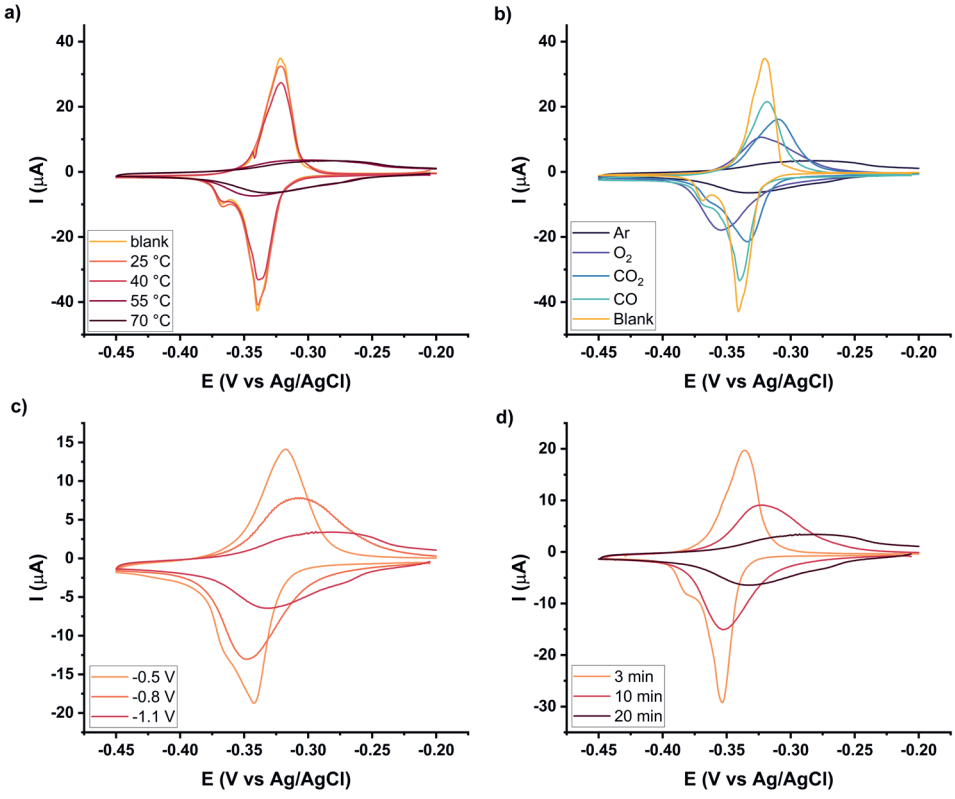

Figure O.1 The Pb UPD CVs under different conditions, all in 0.1 M NaClO4 + 1 mM NaCl + 2 mM PbClO4 pH 3 electrolyte at 5 mV/s. CVs are taken after electrolysis in 0.1 M $KClO_4$ and, if not otherwise specified, at 70 °C in Ar atmosphere at -1.1 V vs RHE for 20 min.

Figures alter one of these parameters a) effect of temperature b) effect of gas composition c) effect of potential of electrolysis and d) effect of time of electrolysis.

In Chapter 3 we showed that the Cu surface is not stable during CO_2 reduction at elevated pressures, as the Pb under-potential (UPD) cyclic voltammogram (CV) changes significantly after electrolysis at these conditions. In a follow-up study, we have looked into this in more detail. The change in the Pb UPD CV of Cu is not caused by CO_2 or bicarbonate because similar behavior is observed in Ar saturated $KClO_4$ electrolyte as shown in Figure O.1a. At room temperatures the Pb UPD CV changes barely and at 40 °C it only changes slightly. However at higher temperatures the CV changes drastically. Figures O.1c and O.1d illustrate that the degree of change not only depends on the temperature but is also time and potential dependent. Moreover, the change in the Pb UPD CV can be suppressed by the gas composition during electrolysis, as shown in Figure O.1b. The change is the largest in an Ar atmosphere, while CO_2, O_2 and especially CO suppress the change in the Cu surface during electrolysis at elevated temperatures. Therefore, our hypothesis is that this change is caused by hydrogen evolution at elevated temperatures. What changes exactly on the Cu surface is still unclear so more research is needed. However, we have indications that the surface changes from mainly Cu(111) to predominantly Cu(110), although it is not the full story and should be confirmed with other techniques.

O.2 Mass transport

In Chapter 4 we showed that mass transport can play an important role in influencing the selectivity towards CO_2 reduction on a Ag catalyst. The similarities between the Ag and the Au catalyst in the H-cell setup indicate that this can be extended to Au and probably other catalysts as well. Previously, Goyal et al.[1] have shown with an RRDE setup that enhanced mass transport indeed influences the selectivity towards CO at the expense of H_2. Faster rotation leads to better mass transport, which lowers the OH^- concentration near the surface. This leads to a lower cation concentration near the surface, resulting in less HER. The activity of the CO2RR towards CO is not influenced by rotation rate and therefore the selectivity increases. However, these experiments have been performed between 800 and 2000 rpm. The experiments in Chapter 4 and Appendix C are performed in an H-cell with a gas flow between 20 and 40 sccm. With ferricyanide experiments we have established that these flowrates translate into rotation rates with an RDE setup of 100-200 rpm. Therefore, we hypothesize that at low rotation rates the effect of mass transport might be opposite to the effect at larger flow rates and HER increases with increasing mass transport. However, this should be studied in more detail and the high-pressure high-temperature cell developed in Chapter 6 is an

ideal setup to do so as this setup allows an RDE setup to be connected to a gas chromatograph. This provides the possibility to study Au at low rotation rates, which is not possible with the RRDE setup employed in Chapter 2, as low rotation rates would lead to too much noise in this setup. Moreover, this also allows to extend the study to other metals such as Ag and Cu, and to study the interdependence of the mass transport and temperature effects on the CO2RR.

O.3 Chain growth mechanism

O.3.1 Chain growth mechanism on Ni

In Chapter 5 we discussed the chain growth mechanism on Ni and in Chapter 7 we showed that this mechanism becomes active on Cu as well at high temperatures and pressures. Moreover, in Chapter 8 we showed that this mechanism is likely to also take place at other metals as Fe, Pd and Cd. However, there is still much unknown about the exact mechanism of the so-called electrochemical Fischer-Tropsch reaction. Therefore, more research is needed to uncover the details of this mechanism. In a preliminary follow-up study of Chapter 5, we have studied the same Ni system under more conditions by changing the electrolyte and reactant. In Chapter 5 we showed that both the activity and chain growth probability differ when CO or CO_2 is used as reactant. In literature, Zhou et al.[2] found that mixing CO and CO_2 would give the highest activity for the chain growth mechanism. However, Figure O.2a and b show that in our system, mixing of CO and CO_2 leads to the mixed results in both activity and chain growth probability. So no optimum is found while mixing both reactants. We also determined the reaction order, which is 0.3 for CO_2 and 1 for CO (between 100 and 70% of CO/CO_2). This indicates that CO is involved in the rate determining step. Experiments changing the buffer concentration

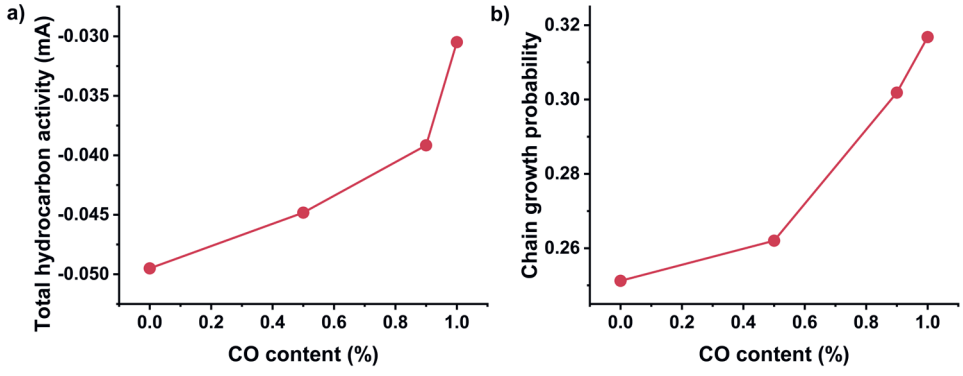

Figure O.2 a) Total hydrocarbon activity and b) chain growth probability during $CO_{(2)}$ reduction with mixed CO CO_2 feeds at -1.175 V vs RHE in 0.1 M pH7 potassium phosphate electrolyte on deposited Ni.

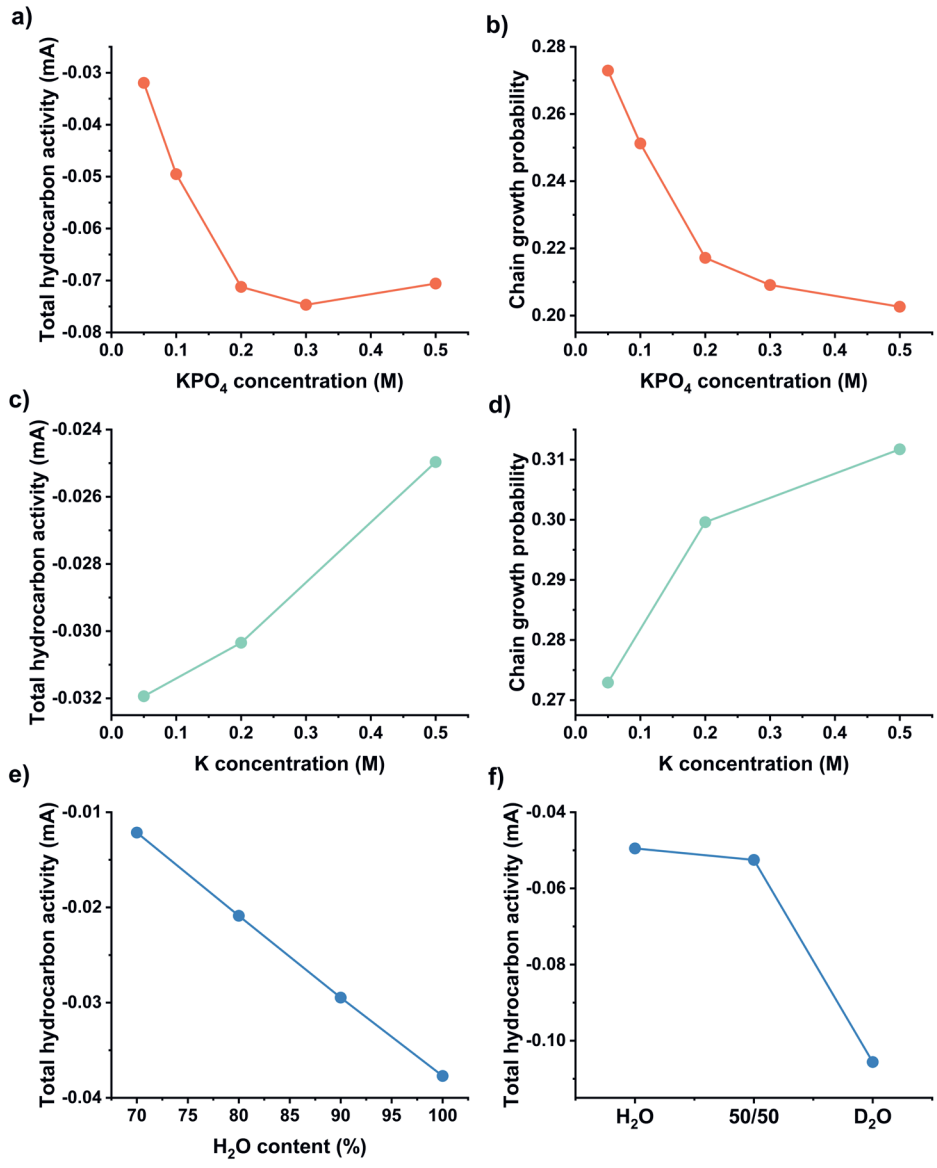

Figure 0.3 a) Total hydrocarbon activity and b) chain growth probability as function of pH7 potassium phosphate concentration at -1.175 V vs RHE on deposited Ni c) Total hydrocarbon activity and d) chain growth probability as function of potassium concentration by adjusting pH 7 0.05 potassium phosphate electrolyte with K_2SO_4. e) total hydrocarbon activity as function of H_2O content adjusted with DMSO in bicarbonate electrolyte and f) total hydrocarbon activity in H_2O, D_2O or mixed electrolyte in phosphate electrolyte

showed that higher phosphate concentrations increase activity and decrease chain growth probability up to 0.2 M after which it plateaus, while cation concentration seems to have the opposite effect, as shown in Figure O.3. The effect of water as proton donor was studied by changing the water content by mixing water with DMSO. This shows that more water leads to a higher activity. However, a kinetic isotope experiment shows a inverse kinetic isotope effect, although mixed H_2O and D_2O experiments show similar results to H_2O. The exact interpretation of the experiments with DMSO and D_2O is still difficult as these different solvents not only change the water concentration but also other parameters. All these preliminary experiments indicate that the rate limiting step is the hydrogenation of CO which is assisted by cations. However, it is still unknown how to exactly interpret the experiments with water to determine its role. Moreover, more experiments are needed to determine if the hydrocarbon chain grows via CH_x coupling, via CO insertion or via a different mechanism. Nickel seems the ideal catalyst to understand this reaction in more detail because of its significant activity, but in a later stage other active catalysts can be studied in more detail as well using the high-pressure high-temperature setup described in Chapter 6.

O.3.2 Chain growth mechanism at elevated temperatures on Cu

Chapter 7 has shown that the C-C coupling mechanism can switch from a CO dimerization or carbonyl coupling mechanism at low temperatures to a chain growth mechanism at high temperatures on Cu. However, some open questions remain. First of all, it would be interesting to study the time dependency in more detail. What happens in the first 30 minutes with the Cu surface and is this related to the initial production of CO? Raman spectroscopy, Pb UPD and SEM experiments can be performed (ex-situ) to gain more insight in the mechanism. For example, if Raman spectroscopy would show coke formation, this would indicate the direct CO dissociation pathway is active. Moreover, experiments changing the electrolyte and CO_2 concentrations as discussed above on Ni could give more insights. An interesting improvement of the setup would be if CO could be used as reactant at elevated pressures, to not only study CO_2 reduction but also CO reduction. Moreover, it would be interesting if a future version of the high-pressure high-temperature electrochemical cell could be coupled to spectroscopy. In that way in-situ spectroscopy could give more insights in the reactions on the surface.

O.4 Further experiments in the high-pressure high-temperature cell

The high-pressure high-temperature setup described in Chapter 6 has shown a lot of potential in Chapter 7 and 8. However, these studies were performed in a short time as the setup was only finished near the end of my PhD. Therefore, we limited these studies to a potassium bicarbonate electrolyte and only a few potentials. This illustrates that a lot of follow-up studies are possible.

First of all, the electrolyte is an important parameter to study as it can significantly influence the CO_2 reduction reaction and more studies are needed to see its effect at elevated pressure and temperature. One could start relatively simple by changing the cation identity from potassium to lithium and cesium or by changing the anion identity from bicarbonate to sulphate or phosphate. Moreover, one could play with the cation and buffer concentrations. Then one could start adding less common salts and molecules to the electrolyte, such as surfactants[3] or organic cations[4], as these have shown to either suppress HER or enhance CO2RR. This all can be done on Cu, to extend the research shown in Chapter 7 and for example see if the chain growth mechanism can be enhanced and optimized on Cu or to suppress HER further at elevated temperatures. However, also the catalysts studied in Chapter 8 can be studied in different electrolytes.

These screened catalysts of Chapter 8 need to be studied in more detail on many different parameters, not only the electrolyte. Due to the large research space, Chapter 8 only studied the metal catalysts at 6 or even 3 combinations of pressure and temperature. However, for the catalyst that are excellent in performing CO2RR such as Ag, Au, Pd, Sn and Pb, another optimum combination of pressure, temperature and potential may exist. This was illustrated by Chapter 6 and 7, where Au and Cu already show very high selectivity for CO2RR and suppression of HER at pressures of a few bar instead of 30 bar in Chapter 8. Therefore, these catalysts should be studied in more detail with smaller temperature and pressure steps and at different potentials as well. It might still be interesting to study some of the inferior CO2RR catalysts (even at elevated temperatures), as they can produce interesting products such as hydrocarbons and methanol. For these catalysts, high pressures seem to be needed, but one could also optimize the temperature and especially the potential and electrolyte.

Besides activity and selectivity, stability is also an important parameter which should be studied in more detail at elevated temperatures. We have shown in Chapter 7 and 8 that Cu, but also other catalysts as Ni and Pd can become unstable at elevated temperatures. Therefore, more research is needed into the causes of these instabilities and strategies have to be developed to enhance the stability. Chapter 4 illustrates that alloying could be a successful strategy in enhancing the

stability at elevated temperatures. Besides stability, alloys could also enhance activity and selectivity. Next to alloying, pulsing could be another possible strategy to increase the stability of the metal catalyst at high temperatures.

Most experiments in this thesis have been performed in an H-cell configuration with simple foil and wire electrocatalysts to keep the studied system as simple as possible and gain fundamental insights. However, it is important to validate these results in other configurations, especially gas diffusion electrodes (GDEs) setups as these are more representative of scaled-up industrial setups.

Lastly, the high-pressure high-temperature setup gives the opportunity to better compare electrocatalysis with thermocatalysis as it allows to go to pressures and temperatures more comparable to thermocatalytic conditions. By combining this with the use of non-aqueous electrolytes and specific substrates for catalysis, one comes closer and closer to the thermocatalytic conditions. On the other hand, thermocatalysis could introduce water and cations to simulate electrocatalytic conditions. By doing this using the same catalyst in both systems, one could build a bridge between thermocatalysis and electrocatalysis and hopefully gain further understanding in the differences and similarities between both and find new ways to control catalytic reaction in the desired way.

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