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The combined effect of temperature and pressure on the electrochemical CO_2 reduction on Cu

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ABSTRACT

Research into the electrochemical CO_2 reduction (CO2RR) is often performed at ambient conditions. However, these are probably not the most industrial relevant conditions, eventually leading to insufficient insights. Using a high-pressure high-temperature electrochemical cell, we have investigated the combined effect of temperature and pressure on the CO2RR on Cu. We show that temperature has a larger effect on the selectivity than pressure and increasing temperature up to 75 °C can increase the C2+ formation. However, stability becomes a bigger issue at higher temperatures, while higher pressures increase the stability as evidenced by the time dependence of the ethylene selectivity. Moreover, elevated pressures can suppress the competing hydrogen evolution reaction and increase both activity and selectivity of CO2RR significantly, even at a few bars of pressure, as long as these pressures are CO_2 pressures and not reached by an inert gas.

1. Introduction

Electrochemical CO_2 reduction (CO2RR) provides a promising approach to convert CO_2 into valuable fuels and chemicals using renewable electricity [1–4]. Of all possible catalysts for this reaction, copper is the only one capable of forming C—C bonds with high Faradaic efficiencies [5–7]. Many factors can influence the CO2RR process on copper and for factors such as electrolyte composition [8–11] and electrode potential [7,10–13], their effects have been well explored. Recently, there has been an increasing focus on the impact of pressure [14–21] and temperature [21–29], which are key parameters that can enhance both the selectivity and activity of CO2RR [14–16,19–23,28,29], unlock new reaction pathways [17,30,31], and improve integration with other industrial processes [17,32–34]. Temperature and pressure are particularly significant because industrial electrolyzers typically operate at higher temperatures [35], to enhance kinetics but also to make use of thermal losses [36–39] or the use of hot feedstocks. However, much of the electrochemical research, including CO_2 reduction studies, is still conducted under conditions of ambient temperature and pressure.

Recently, we have shown the effect of temperature on the activity and selectivity of CO2RR on Cu at ambient pressure [23]. Initially, temperature has a positive effect on both the selectivity and activity towards C2+ products but above an optimum temperature at around 48 °C, the selectivity towards C2+ products and the CO2RR activity decreases with further increasing temperature. This optimum has been recently confirmed by Brandao et al. [29] Ahn et al. [25] observed an optimum in C2+ products as well, although at lower temperatures. Moreover, all abovementioned papers and the earlier work of Hori [26] observed that CH_4 selectivity decreases with increasing temperature, while HER selectivity increases.

Already in the nineties, Hara et al. have studied the effect of pressure on several metal electrocatalysts for CO2RR [14], including Cu [15]. At 1 bar, they observed only HER, but they were able to significantly suppress H_2 formation by increasing the pressure. Moreover, hydrocarbon selectivity was observed to have an optimum around 40 bar. Interestingly, the electrocatalysts studied hardly produced CO and also C2+ products were limited to maximum 7 % selectivity, whereas formic acid selectivity slowly increased with pressure. These older observations are in contrast to recent studies where formate formation dominates at elevated pressures, not only on Cu [16,17,40] but also on Au, Ag and Sn [16]. Interestingly, Girichandran et al. [17] observe 2-propanol as a product at elevated pressures. This product is not found under ambient conditions for CO2RR, as 1-propanol is the preferred product [41]. Proietto et al. [42] show that the FE towards CO2RR does not always rise monotonously but can also show an optimum with pressure, at least for Sn and Ag.

The C2+ formation on Cu at elevated pressures is not studied in

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much detail, although it seems that the dominant C2+ product can change from ethylene into ethanol [20] or acetate [19] at high pressures. Moreover, the C2+ selectivity has sometimes been observed to show an optimum with CO_2 pressure [17]. However, other studies have performed CO reduction at elevated pressures instead of CO2RR and observe a constant increase in C2+ selectivity and activity with increasing pressure [43,44]. This is attributed to an increase in CO coverage, which facilitates CO dimerization and thus the formation of C2+ products. Elevated temperatures have been shown to increase the CO coverage during CO2RR, at least at ambient pressures and temperatures up to 45 °C [23,29]. This illustrates that for CO_2 reduction at elevated pressures there might be a competition between C2+ products and HCOOH formation, which could be influenced with temperature.

Recently, we have developed a special electrochemical system in which both pressure and temperature can be regulated up to 200 °C and 140 bar [45]. On Au electrodes, we have shown that by increasing the pressure, selectivity for CO2RR was significantly improved, especially at elevated temperatures. Moreover, both temperature and pressure can increase the partial current density dramatically. Our system provides the opportunity to study the combined effect of pressure and temperature. In this study, we apply this opportunity to Cu electrodes and show that temperature can improve the selectivity of the traditional CO dimerization mechanism at temperatures up to 75 °C, and that pressure helps to keep the system stable at these temperatures. Elevated pressures can reduce HER activity and selectivity dramatically, even at pressures of only a few bar. However, it is not pressure itself, but specifically CO_2 pressure that enhances CO_2 reduction and C—C coupling.

2. Methods

2.1. Chemicals

The electrolyte was prepared from $KHCO_3$ (99.95 %, Sigma-Aldrich) with Milli-Q water (≥18.2 MΩcm, TOC < 5 ppb) and stored with Chelex (100 sodium form, Sigma-Aldrich) to clean the electrolyte from any metal impurities [46]. H_2SO_4 (95–98 %, Sigma-Aldrich), H_2O_2 (35 %, Merck) and $KMnO_4$ (99 %, Sigma-Aldrich) were used to clean the cells. Ar (5.0 purity, Linde) and CO_2 (4.5 purity, Linde) were used for purging the electrolytes.

2.2. High-temperature high-pressure electrochemical cell

We used an adapted high-pressure, high-temperature cell from Parr instruments; this cell has been described in detail in a recent paper [45] and is shown in Figure S1. The cell was designed to work up to 140 bar and 200 °C. The cell was used in semi-continuous mode, where either CO_2 or a mixture of CO_2 and Ar were constantly purged through the cell. The outlet of the cell was coupled to a condenser and a cooler (Cool--Care, Van der Heijden Labortechnik GMbH) to keep all volatile products in the liquid phase in the setup. The outlet gas was analyzed every 6 min with a Micro-GC from Agilent with two TCD detectors. A combination of a MS6A and a CP-PORABOND Q column was used to detect H_2, CO and CH_4, and an Al_2O_3 column was used to detect the C2 and C3 hydrocarbons. The pressure in the cell was maintained by controlling both the inlet and outlet flow with flow controllers (SLA5850, Brooks Instruments), while for the mixed gas experiments the flow was also checked with a flow meter (Defender 530+, Mesalabs). The temperature was controlled with an electric heating mantle. A homemade two-compartment PEEK cup was used inside the stainless steel chamber and all metal parts from the thermocouple and reference electrode were covered by Teflon tape. Moreover, the lid of the vessel was covered with Viton rubber to prevent any contamination from the stainless steel.

2.3. General electrochemistry

The homemade PEEK cup was cleaned prior to experiments by storing in permanganate solution overnight (0.5 M H_2SO_4, 1 g/L $KMnO_4$). Afterwards, the cell was rinsed, submerged in a diluted mixture of H_2SO_4 and H_2O_2 to remove any traces of MnO_4 and MnO_2, rinsed again and boiled three times with Milli-Q water. A 1 mm thick Cu wire (99.99 %, Mateck) was used as working electrode. Before experiments, the working electrode was electropolished in 85 % H_3PO_4 (Suprapure, Merck) by applying +3 V versus a graphite counter electrode for 20 s and subsequently rinsed with Milli-Q water. Due to the large difference in current at the various conditions used, 4 different sized wires were used to ensure the current stays between 10 mA (for product detection) and 200 mA (for stability of the system) during the experiment. The areas of the different working electrodes were normalized using their double layer capacitance, measured from −0.3 to 0.2 V vs SHE at scan rates from 200 to 1400 mV/s [47]. The areas of the electrodes can be found in Table S1.

During experiments, a DSA counter electrode (Magneto) was separated from the working and reference electrode by a PiperION membrane (A40, Versogen) [48,49]. The experiments were performed with a Gamry Interface 1010B potentiostat and current interrupt [50] was used to correct for the Ohmic drop. Experiments were performed for 60 or 90 min at constant potential. Gaseous products were determined every 6 min with GC as described above, while liquid products were determined afterwards by sampling the 65 ml catholyte and analyzing this using high performance liquid chromatography (HPLC, Shimadzu) with an Aminex HPX-87H column (Bio-rad). During experiments the pressure was maintained within an error of 0.1 bar, while temperature was maintained within an error of 2 °C. Before reaching the conditions used for the experiment (which typically takes up to an hour), the working electrode was always under potential control at a potential of −0.8 V vs Ag/AgCl.

2.4. Reference electrode corrections

In this study, all potentials are reported vs SHE(T). During experiments, an Ag/AgCl electrode (Ultradeg, 0.1 M KCl, Corr Instruments) was used as a reference electrode. However, with changing temperature, one should make several corrections to convert the potential from Ag/AgCl to SHE. The Nernst equation is used to determine the shift of the Ag/AgCl reference electrode against SHE:

$$E_{Ag/AgCl} = E^0_{Ag/AgCl}(T) - \frac{\ln(10) * RT}{nF} * \log(a_{Cl^-}(T)) \tag{7.1}$$

with E^0 being the standard potential, R the gas constant, T the temperature, n the number of electrons, F Faradays constant and $a_{Cl\text{-}}$ the activity of the chloride anion. The standard potential of Ag/AgCl vs SHE is a function of temperature and can be calculated using the following formula[51]:

$$E^0_{Ag/AgCl}(T) = -0.111658 + 0.011134 * T - 0.001757268 * T * \ln(T) \tag{7.2}$$

The temperature dependence of the activity of the chloride ions can be determined from a formula from Bogaerts et al.[52]:

$$a_{Cl^-}(T) = exp\left[\log(a_{Cl^-}(25\,^\circ C)) - \frac{\sqrt{I_{Cl^-}}}{1+\sqrt{I_{Cl^-}}} * \left(A_\gamma^T - A_\gamma^{25\,^\circ C}\right)\right] \tag{7.3}$$

where $a_{Cl\text{-}}$ is the activity of the chloride anion at room temperature [53], I_{Cl} is the ionic strength of the chloride anion, and A_γ is the Debye-Huckel parameter [52].

With these formulas, the shift between an Ag/AgCl reference and SHE could be determined at different temperatures as shown in Table S2. Even though the SHE potential is defined as zero at all temperatures, there is a difference in potential between SHE(T) and SHE (25 °C) [54]. One could correct for this difference too, but we decide to limit the corrections to the necessary corrections and therefore report on a SHE(T) scale. In previous studies we reported on the RHE(T) scale

[22–24,55], but in this study the potential could not be reported vs. RHE because the pH should be known to convert SHE to RHE. However, it was for us impossible to measure the exact pH of the electrolyte at elevated CO_2 pressures and temperatures.

3. Results and Discussion

3.1. Screening temperature, pressure and potential

As the research space increases tremendously when pressure and temperature are varied as parameters, we first screened the effect of these parameters at different potentials. We mainly focused on −1.4 V vs SHE as shown in Figures 1 and S2. This potential corresponds to −1.0 V vs RHE at ambient conditions in 0.2 M $KHCO_3$, a potential which is commonly used for electrochemical CO_2 reduction on Cu. However, we also performed screening experiments at −1.3 and −1.5 V vs SHE (Figure S3 and S3), as the potential can change the effects of temperature and pressure [22,55]. Moreover, all experiments have been performed in 0.2 M $KHCO_3$ because changing the electrolyte as well would increase the research space beyond reasonable measure.

Fig. 1 shows that temperature has a more significant effect on the selectivity (towards the major products hydrogen, carbon monoxide, formic acid, methane, ethylene, and ethanol) than pressure. With increasing temperature, more H_2 is generated and the selectivity for all CO2RR products decreases. With increasing pressure, this H_2 enhancing effect of temperature can be suppressed and the CO2RR stays active up to higher temperatures. At room temperature, there are only subtle effects on the selectivity, while the effect of pressure becomes more clear at 50 and 75 °C. These trends can also be observed at the other potentials. The exact values of the FE for the different products depends on the potential applied, but the overall trends for temperature and pressure seem independent of potential, at least in this potential window. Figure S2 shows the 2D maps for the minor products (methanol, acetate, ethylene glycol, acetaldehyde, propionaldehyde, propanol). In general, the trends are similar to the major products in Fig. 1, however the effect of pressure at room temperature is more clear, especially for methanol and acetate. Acetate and ethylene glycol seem to form even at very high temperatures.

3.2. Effect of temperature

The screening data shows that the most interesting parameters to study the C2+ formation in more detail are at −1.5 V vs SHE at temperatures up to 75 °C. Therefore, these conditions have been studied in more detail with an improved setup in pure CO_2. Figures S5–7 show the effect of temperature on the activity and selectivity on Cu at different pressures. The trends at ambient pressure are comparable to the trends we reported before in a different setup [23], although not exactly the same. In general, HER selectivity increases with temperature, while the selectivity towards methane, HCOOH and CO decrease with increasing temperature. However, previously an optimum in C2+ formation was observed around 50 °C, which is now not the case at 1 bar but only at elevated pressures. In previous work we have discussed several contributions to this temperature optimum, of which the CO_2 bulk concentration, which decreases with increasing temperature, is the main one affected by increasing the pressure.

To look into these differences in C2+ formation in more detail and illustrate more specifically the effect of temperature and time, Figs. 2 and S8 show the selectivity towards C_2H_4 as a function of temperature and electrolysis time. Initially, at 1 bar, the effect of temperature is very similar to what we reported before [23]. There is an optimum in ethylene selectivity at ca. 50 °C. However, in the setup used in this work the Cu seems to be less stable than in the setup used previously, and with time the selectivity towards ethylene decreases, resulting in a negative trend with temperature over the entire experiment. The electrochemical cell used here is very different to the design used previously [23], for example the membrane, reference and electrolyte volume are different. Any of these aspects might influence the stability, but also the fact that the working electrode is now a wire instead of a disk. Additionally, the increased electrolyte concentration might also cause part of the differences in stability.

Pressure also influences the effect of temperature as at elevated pressures the FE towards ethylene decreases less with time compared to 1 bar. More interestingly, after 20 min, the selectivity towards ethylene

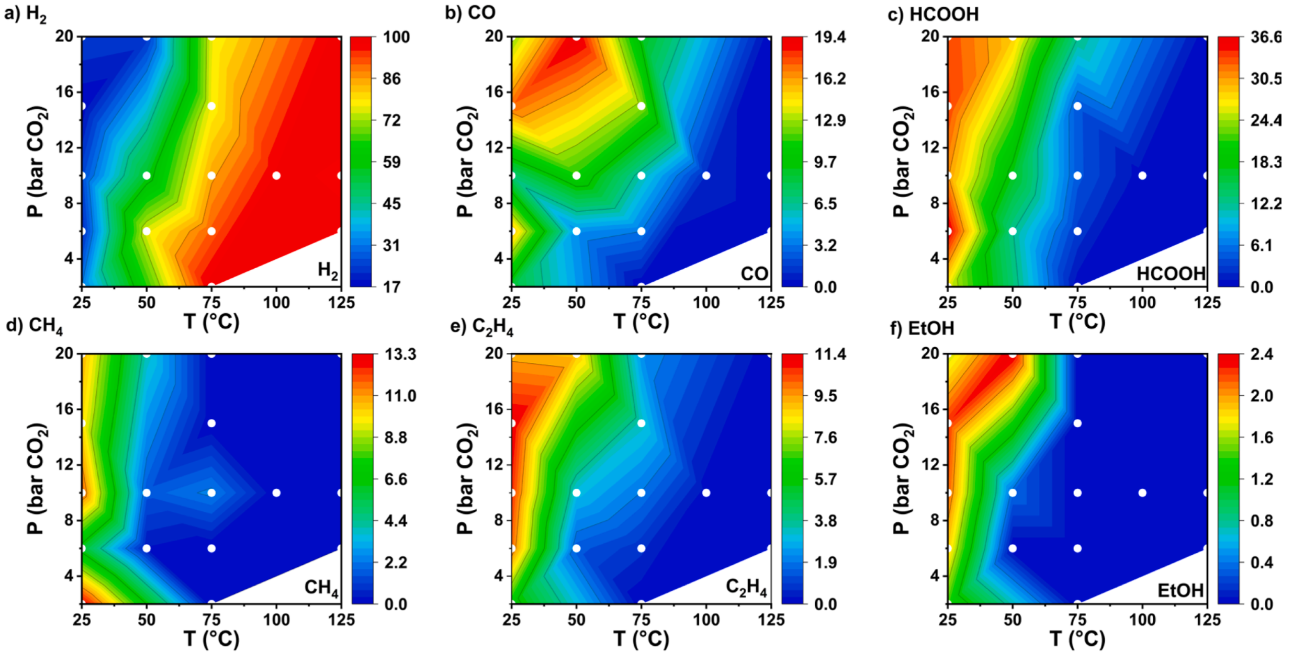

Fig. 1. Faradaic efficiency towards the main CO2RR products as function of temperature and pressure at −1.4 V vs SHE in 0.2 M $KHCO_3$ with a 50/50 ratio of CO_2 and Ar. The white dots give the measured data points and the maps are constructed via interpolation between these points. FE for a) hydrogen b) carbon monoxide c) formic acid d) methane e) ethylene and f) ethanol.

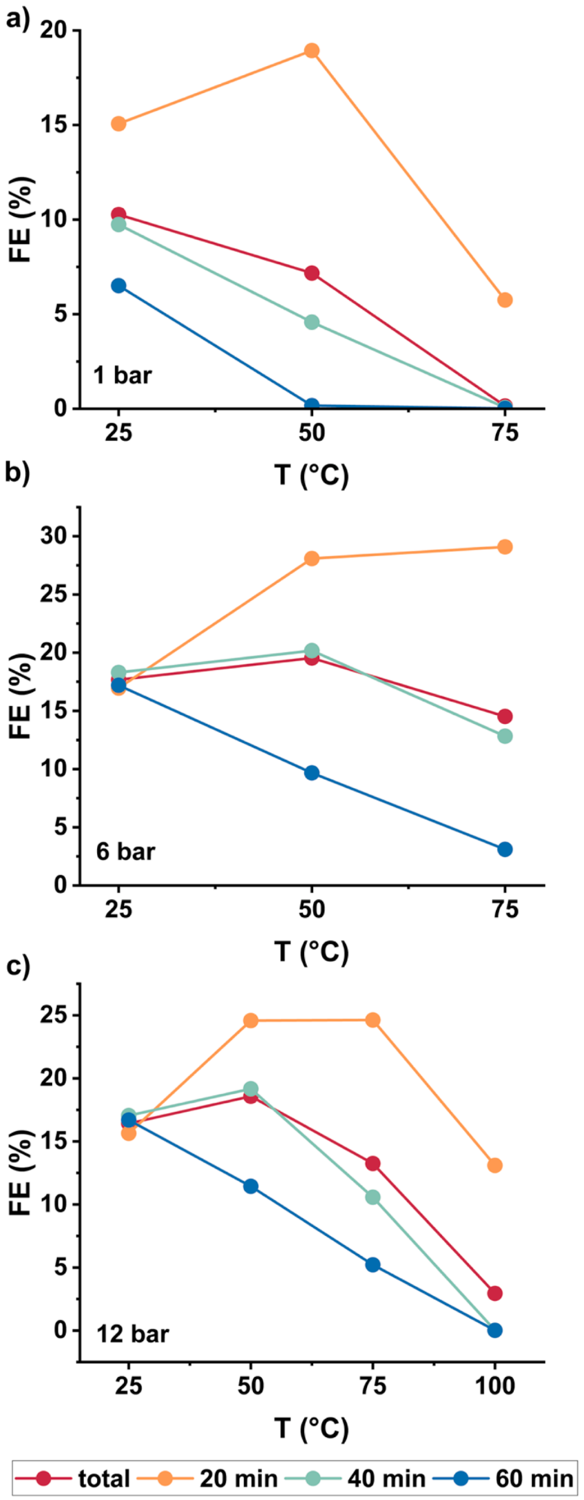

Fig. 2. Faradaic efficiency towards ethylene as function of temperature after different electrolysis times at −1.5 V vs SHE in 0.2 M $KHCO_3$ at a) 1 bar b) 6 bar and c) 12 bar.

remains high, even up to temperatures of 75 °C. This shows that even a few bars of elevated pressure can enable the formation of C2+ products at higher temperatures, most likely because the CO_2 concentration in the electrolyte is maintained at a reasonable concentration (as shown by Figure S9), which could influence the CO coverage. However, a reasonable CO_2 concentration in itself is not sufficient to maintain high FE towards ethylene. At 100 °C and 12 bar, the CO_2 bulk concentration is higher than at 75 °C and 6 bar, however the FE towards ethylene is lower.

We look in more detail at the effect of temperature and pressure on the stability of the Cu electrocatalyst in Fig. 3. This figure shows the selectivity towards ethylene at 40 and 60 min, plotted as a ratio compared to the initial FE at 20 min, as a descriptor for stability. This figure clearly shows that the ethylene selectivity on Cu becomes less stable with increasing temperature. We have shown that in the setup used in this study, no contamination such as Fe or Ni can be found that would explain the decrease in ethylene with time [31] . However, in previous study we have shown that the Cu surface deactivates at elevated temperatures, with the surface getting more smooth at elevated temperatures, which might cause this instability in ethylene formation [23]. Interestingly, increasing the pressure, at a given temperature, generally increases the stability of ethylene formation. To make CO2RR on Cu feasible on an industrial scale, it is important to stabilize Cu at temperatures up to at least 75 °C, which are reasonable industrial operation temperatures [56,57]. We hypothesize that the stabilization of Cu through pressure is due to the suppression of HER and an increase of the coverage of CO_2 and/or CO. However, additional strategies are probably needed to obtain truly long term stability of the Cu catalyst at elevated temperatures. Some possible strategies may include pulsing of the potential or alloying the Cu electrode to make it more stable at high temperatures [55].

3.3. *Effect of pressure*

Pressure does not only influence the stability of the Cu catalyst or increase the operating temperature window, but can itself also affect the activity and selectivity of the CO2RR. Fig. 1 showed that the effect of pressure on the selectivity is smaller than the effect of temperature, but it is not negligible. Fig. 4 shows the effect of pressure on the selectivity of the major products during CO2RR at −1.5 V vs SHE at room temperature, while the effect on the minor products is shown in Figure S23. The pressure has been increased both with CO_2 and with Ar to be able to distinguish between the effect of pressure itself and of CO_2 pressure specifically.

Figure 4 and S9 show that increasing CO_2 pressure can decrease the selectivity towards H_2 and that this effect already plateaus at a relatively low pressure of 3 and 6 bar at 25 and 75 °C, respectively. This same pressure is the optimum pressure for C_2H_4 selectivity, and for C2+ selectivity in general. At 25 °C, the initial pressure increase from 1 to 3 bar leads to a rapid increase in C2+ selectivity, but with further increasing pressure, the selectivity towards C2+ slowly decreases in favor of the simple C1 products CO and HCOOH (although the selectivity of the minor C2+ liquid products does keep increasing with increasing CO_2 pressure). Even though the selectivity towards HCOOH increases slightly at high pressures, we never observe very selective CO2RR towards HCOOH as described in some literature studies [16,17], although others did not observe this effect [42]. This difference could possibly be attributed to the differences in electrolyte pH [19], although Figure S24 indicates that simply a difference in electrolyte concentration between these studies does not explain the differences in HCOOH behavior with pressure. Possibly the observed differences could be ascribed to the electrode morphology as both references 16 and 17 use a copper foam working electrode, which could influence for example the local pH very differently than our Cu wire working electrode.

During CO reduction on Cu, a continuous increase in C2+ selectivity with increasing pressure was observed [43,44], which was attributed to the increasing *CO coverage. However, Fig. 4 shows this is not the case for CO_2 reduction, especially at higher pressures of 20 bar. It would be interesting to compare CO_2 and CO reduction at elevated pressures and temperatures but unfortunately, due to safety concerns, we are not able to perform CO reduction experiments at elevated pressures at this moment. Moreover, it would also be interesting to follow spectroscopically the *CO coverage during CO2RR at elevated pressures, which is

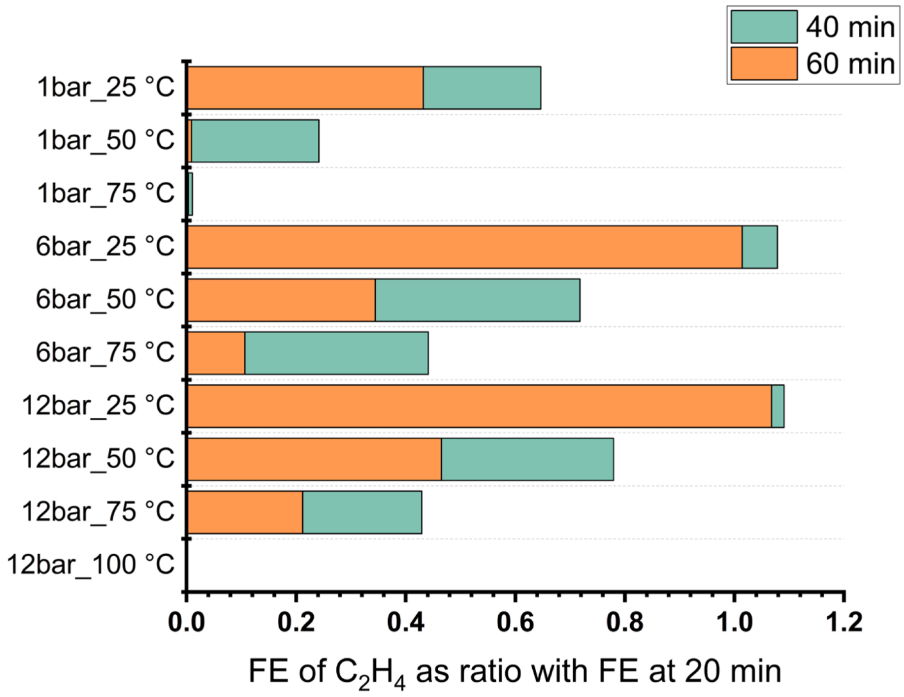

Fig. 3. Stability of ethylene formation as function of temperature and pressure. Stability of ethylene formation is here defined as the FE that remains after 40 and 60 min compared to the FE at 20 min at a given condition.

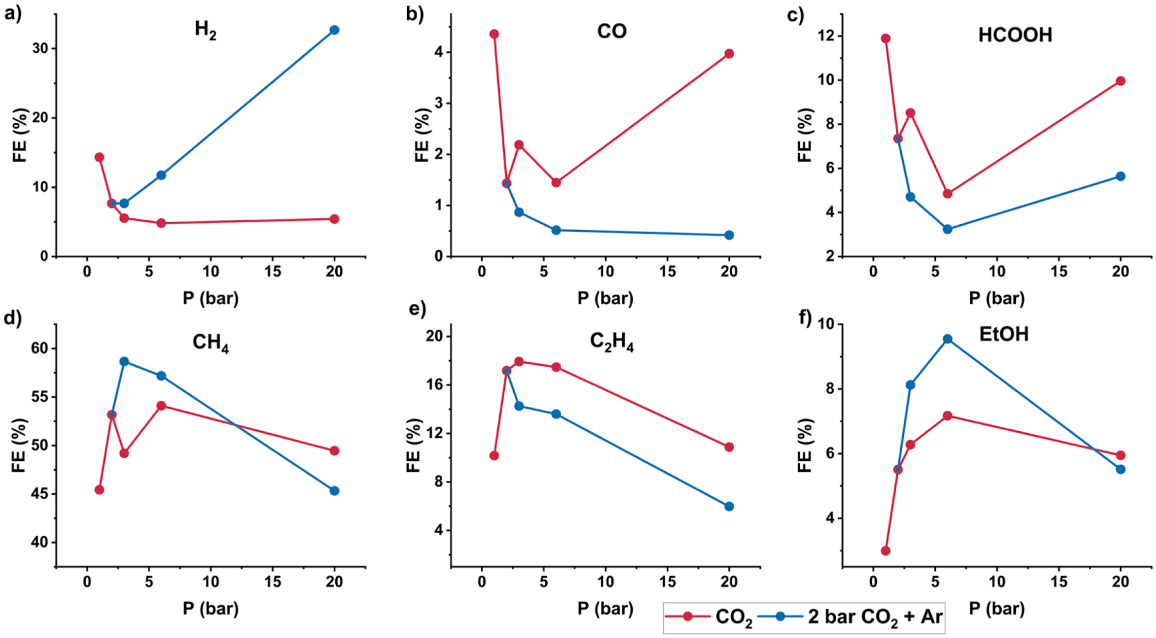

Fig. 4. Faradaic efficiency towards the main CO2RR products as function of CO_2 and total pressure at −1.5 V vs SHE in 0.2 M $KHCO_3$ at 25 °C. Red lines are performed in pure CO_2 and blue lines are at 2 bar of CO_2 and pressure is increased with Ar. FE for a) hydrogen b) carbon monoxide c) methane d) formic acid e) ethylene and f) ethanol. Note that the (single) data point at 3 bar in b), c) and d) seems somewhat of a (random) outlier, but it does not interfere with the main trend.

unfortunately not possible with our current setup. However, from the product analysis, we hypothesize that the *CO coverage does not continuously increase with increasing CO_2 pressure, which might be due to faster desorption of CO due to increased CO_2 adsorption [45,58]. This limit in *CO coverage would explain the observed optimum in C2+ products at relatively low pressure and shift to simple C1 products with higher pressure.

Fig. 4a demonstrates that the suppression of H_2 at elevated pressures is due to the increase in CO_2 pressure. When the pressure is increased with Ar instead of CO_2, the FE towards H_2 increases at 25 °C, although at elevated temperatures Ar pressure does suppress HER slightly (Figure S12a). This might be due to the very high initial HER selectivity of >90 % or the improved stability, even under Ar pressure. Moreover, when Ar is used to increase the pressure, most CO2RR products show lower selectivities than in a pure CO_2 atmosphere, as shown in Figure 4 and S9. For ethanol and methane this is not the case at intermediate pressures of 3–6 bar, but also for these products the activity is lower with Ar than in a pure CO_2 atmosphere, as shown in Figure S11 and S13.

Therefore the increase in selectivity for these two CO2RR products is due to a relatively smaller decrease in activity compared to for example ethylene. If the system is ideal and Ar would be completely innocent, it would be expected that increasing the Ar concentration while keeping the CO_2 partial pressure constant would have no impact at all as the adsorption and kinetics should not be affected. However, Figures 4 and S11 show that CO2RR performance decreases while HER is enhanced when the Ar pressure is increased. Therefore, the CO_2 partial pressure is not the only contributing factor, but there seems to be some dilution effect as well. However, it is impossible to completely decouple this dilution effect from the effect of the CO_2 partial pressure.

Figures 4 and S12 illustrate that the main reason for suppression of HER is not pressure itself, but CO_2 pressure, although Ar pressure might slightly help at elevated temperatures when HER is very active. We hypothesize that the HER suppression is due to competition of adsorption sites between CO2RR and HER intermediates, where elevated CO_2 pressures lead to a blockage of adsorption sites for HER [45].

4. Conclusion

In this study we have investigated the combined effect of pressure and temperature on the electrochemical CO_2 reduction on Cu. We show that temperature has a larger effect on the selectivity than pressure, although the effect of the latter is not negligible. Increasing the temperature can increase the FE towards traditional C2+ products and increasing the pressure can broaden the temperature range in which Cu catalysts can operate, both by increasing the CO_2 available and the Cu stability. At ambient temperature, increased CO_2 pressure itself can significantly suppress the competing hydrogen evolution reaction, even at a few bar. It is important to make the distinction between pressure and CO_2 pressure, as these do not have the same effect on the CO2RR. For positive effects, it is in most cases crucial to increase the CO_2 (partial) pressure and not just the total pressure in the system.

This study has shown the importance of studying the effect of temperature and pressure. However, due to the large parameter space, more avenues should be explored, for example to the effect of other parameters such as electrolyte composition in combination with temperature and pressure. We also highlight the importance of studying the stability of the Cu electrocatalysts, especially at elevated temperatures, beyond simply the stability of ethylene formation, as was done here. Alloying Cu with more stable metals or pulsed experiments are examples of possible ways to increase both the stability of ethylene formation and the Cu catalyst itself. Furthermore, CO reduction instead of CO_2 reduction as well as experiments in different systems such as a flow cell and using a gas diffusion electrode at both elevated pressures and temperatures are interesting and important to gain more insight into the combined effects of pressure and temperature.

CRediT authorship contribution statement

Rafaël E. Vos: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization. **Daniel Schauermann:** Validation, Investigation. **Marc T.M. Koper:** Conceptualization, Resources, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2026.148199.

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