

Scale-up Effects on the Mechanisms of the Electrochemical Synthesis of Anhydrous Formaldehyde

Einfluss der Skalierung auf die Mechanismen der elektrochemischen Synthese
von wasserfreiem Formaldehyd

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The only difference between screwing around and science is writing it down.

- Alex Jason

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Auch wenn eine Dissertation am Ende die Leistung einer einzelnen Person widerspiegelt, so ist sie meist doch ein Ergebnis von vielen zusammengetragenen Ideen. So ist es auch bei meiner Arbeit, die durch die Unterstützung meiner Kollegen, Freunde und meiner Familie mitgeprägt wurde. Euch gilt mein Dank.

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Abstract

We currently face the consequences of human-induced climate change. To reduce greenhouse gas emissions, our society has to transition from the use of fossil resources to sustainable ones. Industrial processes are often driven by thermal energy that is obtained by burning fossil fuels. However, sustainable energy is mainly generated in the form of renewable electricity. Instead of converting renewable electricity into thermal energy, it can be used directly as the driving force for the industrial process. The direct use of electricity requires changes within industry, especially in the chemical industry. One approach to more sustainable industrial syntheses are their electrification. For example, the platform chemical formaldehyde is industrially synthesized at high temperatures. Formaldehyde can also be obtained electrochemically from aqueous methanol at low temperatures. Yet, the efficiency of the electrochemical formaldehyde formation suffers from complete methanol oxidation and other side reactions that are enabled by water activation. Water activation can be avoided by using anhydrous electrolyte solutions. Only a few studies using anhydrous methanol for the electrochemical formaldehyde synthesis have been reported. These experiments were performed at laboratory scale; most lack complete experimental documentation; and used, by today's standards, invalid reference electrodes.

In this work, the electrochemical oxidation of anhydrous methanol to formaldehyde is investigated with respect to its scalability and industrial application. A suitable and reliable reference electrode was developed to enable accurate potential control under anhydrous reaction conditions. Several electrode materials were investigated in a batch cell for their activity and selectivity in the conversion of anhydrous methanol to formaldehyde. The reaction was transferred to an electrochemical flow cell to investigate its performance depending on the flow cell parameters (anode size and support, flow rate, electrode gap, and temperature) and at elevated current densities. Previously identified active electrode materials were tested under these conditions for their stability. Only platinum was stable at high current densities and reached Faraday efficiencies of up to 90 %. All parameters have a significant influence on the reaction performance. In particular, the electrode gap has the largest influence on the energy requirements, which are limited by the electrolyte conductivity. A more in-depth analysis of the physical and chemical electrolyte properties allows a correlation between the electrolyte and effect on the reaction. The formaldehyde synthesis occurs via different reaction mechanisms depending on the electrolyte composition.

Because of the reaction's stable performance at elevated current densities, it has the potential to be applied industrially. Further understanding of the influences of the electrolyte composition on the reaction mechanism is required to optimize the reactor design for further scale-up.

Zusammenfassung

Wir sind derzeit mit den Folgen des vom Menschen verursachten Klimawandels konfrontiert. Um die Treibhausgasemissionen zu verringern, muss die Gesellschaft von der Nutzung fossiler Ressourcen auf nachhaltige Ressourcen umstellen. Industrielle Prozesse werden häufig durch thermische Energie angetrieben, die durch die Verbrennung fossiler Brennstoffe gewonnen wird. Nachhaltige Energie wird jedoch hauptsächlich in Form von erneuerbarer Elektrizität erzeugt. Anstatt erneuerbare Elektrizität in Wärmeenergie umzuwandeln, kann sie direkt als Antriebskraft für den industriellen Prozess genutzt werden. Die direkte Nutzung von Strom erfordert Veränderungen in der Industrie, insbesondere in der chemischen Industrie. Ein Ansatz für nachhaltigere industrielle Synthesen ist deren Elektrifizierung. So wird beispielsweise die Plattformchemikalie Formaldehyd industriell bei hohen Temperaturen synthetisiert. Formaldehyd kann auch elektrochemisch aus wässrigem Methanol bei niedrigen Temperaturen gewonnen werden. Die Effizienz der elektrochemischen Formaldehydbildung leidet jedoch unter der vollständigen Methanoxidation und anderen Nebenreaktionen, die durch Wasseraktivierung ermöglicht werden. Die Wasseraktivierung kann durch die Verwendung wasserfreier Elektrolytlösungen vermieden werden. Es gibt nur wenige Studien über die Verwendung von wasserfreiem Methanol für die elektrochemische Formaldehydsynthese. Diese Experimente wurden im Labormaßstab durchgeführt; den meisten fehlt eine vollständige experimentelle Dokumentation und es wurden nach heutigen Maßstäben ungültige Referenzelektroden verwendet.

In dieser Arbeit wird die elektrochemische Oxidation von wasserfreiem Methanol zu Formaldehyd im Hinblick auf ihre Skalierbarkeit und industrielle Anwendung untersucht. Es wurde eine geeignete Referenzelektrode entwickelt, die eine genaue Potenzialkontrolle unter wasserfreien Reaktionsbedingungen ermöglicht. Es wurden mehrere Elektrodenmaterialien in einer Batch-Zelle auf ihre Aktivität und Selektivität bei der Umwandlung von wasserfreiem Methanol zu Formaldehyd untersucht. Die Reaktion wurde in eine elektrochemische Durchflusszelle transferiert, um ihre Leistung von den Flusszellenparametern (Anodengröße und -träger, Durchflussrate, Elektrodenabstand und Temperatur) sowie bei höheren Stromdichten zu untersuchen. Zuvor identifizierte aktive Elektrodenmaterialien wurden unter diesen Bedingungen auf ihre Stabilität getestet. Nur Platin war bei hohen Stromdichten stabil und mit Faraday-Effizienzen von bis zu 90 %. Alle Parameter haben einen erheblichen Einfluss auf die Reaktionsleistung. Der Elektrodenabstand hat den größten Einfluss auf den Energiebedarf, der durch die Leitfähigkeit des Elektrolyten begrenzt wird. Eine eingehendere Analyse der physikalischen und chemischen Elektrolyteigenschaften ermöglicht eine Korrelation zwischen dem Elektrolyten und seinem Reaktionseinfluss. Die Formaldehydsynthese erfolgt je nach Elektrolytzusammensetzung über unterschiedliche Reaktionsmechanismen.

Aufgrund der stabilen Effizienz der Reaktion bei hohen Stromdichten hat die Reaktion das Potenzial, industriell eingesetzt zu werden. Ein besseres Verständnis der Einflüsse der Elektrolytzusammensetzung auf den Reaktionsmechanismus ist erforderlich, um das Reaktordesign für eine weitere Hochskalierung zu optimieren.

Contributions

Parts of this thesis have been published.

- F. Schwarz, E. Larenz, A. K. Mechler, Sustainable electrochemical synthesis of dry formaldehyde from anhydrous methanol. *Green Chemistry* **2024**, *24*, 4645-4652. DOI: 10.1039/D3GC04978G
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- Mae Mckenna, Electrochemical Synthesis of Formaldehyde from Anhydrous Methanol. 2021, project report.
- Anne Liang, Identification of suitable reference electrodes for partial oxidation of anhydrous Methanol, 2022, Bachelor thesis.
- Liliana Wuerth, Investigation into the use of electrochemical flow cells for the anhydrous oxidation of methanol into formaldehyde, 2022, project report.
- Elizabeth Larenz, Electrooxidation of Anhydrous Methanol to Formaldehyde: Investigation of the Catalytic Activity of Transition Metal Electrode Materials

and Optimization of Reaction Conditions, 2023, Master thesis.

- Sophia Hohlfeld, Investigation of the influence of different reaction parameters on the concentration of formaldehyde during the electrochemical oxidation of anhydrous methanol, 2024, Bachelor thesis.
- Nina Nagel, Influence of the electrolyte on the anhydrous methanol oxidation to formaldehyde, 2025, project report.

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Nomenclature

Abbreviations

A	Acid
a.u.	Arbitrary unit
AC	Alternating current
AN	Acceptor number
at.	Atom
ATR-SEIRAS	Attenuated total reflection surface-enhanced infrared adsorption spectroscopy
B	Base
C	Capacitor
CA	Chronoamperometry
CE	Counter electrode
CV	Cyclic voltammetry
DC	Direct current
DMF	Dimethylformamid
DMFC	Direct methanol fuel cell
DMSO	Dimethyl sulfoxide
DN	Donor number
EIS	Electrochemical impedance spectroscopy
el	Electrolyte
fc	Ferrocene
GDE	Gas diffusion electrode

HER	Hydrogen evolution reaction
HPLC	High performance liquid chromatography
HSAB	Hard and soft acids and bases
IR	Infrared
J	Junction
LJP	Liquid junction potential
MeOH	Methanol
MOR	Methanol oxidation reaction
OCP	Open circuit potential
RE	Reference electrode
RHE	Reversible hydrogen electrode
RT	Room temperature
SCE	Saturated calomel electrode
SEM	Scanning electron microscopy
TBAP	Tetrabutylammonium perchlorate
UV	Ultraviolet
WE	Working electrode
wt.	Weight

Indices

c	cutoff
cell	electrochemical cell
corr	corrected
fin	final
init	initial
prod	produced
theo	theoretical

Symbols

δ	Partial charge	—
$\Delta_{\text{f}}H^0$	Enthalpy of formation, standard	kJ mol^{-1}
$\Delta_{\text{solv}}G^0$	Gibbs free energy of solvation, standard	kJ mol^{-1}
ϵ_0	Vacuum permittivity	$\text{C}^2 \text{kg}^{-1} \text{m}^{-3} \text{s}^2$
ϵ_{r}	Relative permittivity	—
κ	Conductivity	S cm^{-1}
μ	Viscosity	Pa s
ν_{p}	Stoichiometric factor	—
ϕ	Faraday efficiency (FE)	—
ϕ_{a}	Phase angle	$^{\circ}$
$\tilde{\nu}$	Wavenumber	cm^{-1}
$\vec{\mu}$	Dipole (given in Debye (D))	$10^{-18} \text{cm}^{5/2} \text{g}^{1/2} \text{s}^{-1}$
A	Area	cm^2
a	Activity	—
c	Concentration	mol L^{-1}
d	Distance	m
E	Potential	V
e	Elementary charge	$1.60 \times 10^{-19} \text{C}$
$E_{1/2}$	Half-wave potential	V
E_{ion}	Ionic potential loss	V
E_{s}	Specific energy consumption	kW h kg^{-1}
F	Faraday constant	C mol^{-1}
f	Frequency (often given in Hertz (Hz))	s^{-1}
H	Enthalpy	kJ mol^{-1}
I	Current	A
i	Current density	A cm^{-2}
K_{a}	Acid dissociation constant	—

Nomenclature

K_b	Base dissociation constant	—
K_w	Auto-dissociation constant of water	—
M	Molar mass	g mol^{-1}
n	Amount of substance	mol
N_A	Avogadro constant	$6.02 \times 10^{23} \text{ mol}^{-1}$
n_r	Refractive index	—
$pp.$	Percentage point	—
Q	Electric charge	C
R	Resistance	Ω
r_i	Ionic radius	m
R_u	Uncompensated resistance	Ω
T	Temperature	K
t	Time	s
U	Voltage	V
V	Volume	L
Z	Impedance	Ω
z	Number of electrons	—
Z'	Resistance (ohmic)	Ω
Z''	Reactance (capacitive and inductive)	Ω
z_i	Charge of ion	—
j	Imaginary	—

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1 Introduction

The effects of climate change are increasing in frequency and severity. New developments in climate models allow the attribution of extreme weather and climate-related events to human influence.^[1] More than half of these events in 2021 and 2022 are attributed to human influence or are likely influenced by it.^[2] The human influence on climate is mainly rooted in the emission of greenhouse gases, e.g., CO₂, CH₄ and water vapor.^[3] To tackle the current challenges, humanity needs to adjust its way of life. One publicly and scientifically discussed approach to reducing the greenhouse gas emissions is to switch to more sustainable modes of transportation.^[4–6] Not only does our mobility depend on burning fossil fuels, but many industrial processes are also driven by thermal energy, such as the Haber-Bosch process or steelmaking.^[7,8]

Instead of thermal energy obtained from burning fossil fuels, sustainable energy sources, such as solar, wind, or water, generate electricity. It is possible to use the generated electricity directly as the driving force for chemical reactions.^[9] The electrification of industrial-scale chemical synthesis can lead to overall more energy-efficient processes. One large-scale industrial process is the methanol oxidation to formaldehyde, an essential C1 building block for the chemical industry, with a worldwide production of 45.6×10^6 t in 2020.^[10] All established industrial processes work with methanol feedstock and require elevated temperatures of 250–720 °C.^[11] The methanol feedstock is synthesized via syngas (CO + H₂), which is obtained from fossil resources.^[12] Pure formaldehyde is a colorless gas at ambient temperature, but in industrial processes, formaldehyde is obtained as an aqueous solution. Because of its high reactivity, formaldehyde is used as an intermediate for a variety of fine chemicals such as 1,4-butanediol, pentaerythritol, and 4,4'-diphenylmethane diisocyanate.^[11] The majority of formaldehyde is used to directly synthesize polymers and resins, such as phenol formaldehyde resin, urea formaldehyde, and polyoxymethylene. Phenol formaldehyde resin and urea formaldehyde belong to the most widely used thermosetting polymers while polyoxymethylene is a commonly used thermoplastic polymer. These cheap and adaptable polymers find use in machinery and vehicle construction, electrical engineer-

ing, lacquers and glues, construction, mining and furniture manufacturing.^[13] Because of its versatile use cases, formaldehyde is an essential C1 building block for the chemical industry.

There are two main approaches to make the formaldehyde synthesis more sustainable: the use of carbon neutral methanol and the electrification of the process. For carbon neutral methanol feedstock, CO₂ can be captured from industrial off-gases or air^[14,15] and recycled via CO^[16–19] or directly to methanol.^[20–23] The reduction of CO₂ to formaldehyde is also investigated but has not been achieved on a significant scale yet.^[24,25] The highly reducing reaction environment necessary for the CO₂ reduction also reduces formaldehyde to methanol.^[25] Thus, it seems unlikely that the required formaldehyde quantities can be synthesized directly from CO₂, and the synthesis will continue via methanol, ideally from a renewable source. The electrification of the process allows for the direct energy use from a renewable source without losses due to conversion to heat. The use of electricity as the driving force enables different reaction paths compared to thermally-driven processes, which often permits milder reaction conditions, e.g., ambient temperature.^[9]

Formaldehyde can be produced electrochemically as it was found as a side product in direct methanol fuel cells in which aqueous methanol is oxidized to CO₂.^[26–31] These reports show that the formaldehyde formation and selectivity are highly dependent on the reaction conditions. Recently, the electrochemical synthesis of formaldehyde based on aqueous methanol was reported with a Faraday efficiency of 58 %.^[32] However, the presence of water enables subsequent oxidation to formic acid and CO₂, which lowers the reaction’s efficiency.^[33] These side reactions can be minimized by using anhydrous methanol. Literature from the 1960s and 70s reports formaldehyde as the main product on Pt electrodes with Faraday efficiencies of approximately 75 %.^[34–37] Yet, these Faraday efficiencies were measured at small current densities (3.3 mA cm^{−2})^[34] and in small-scale (wire electrode) setups.^[36] For industrial application, high current densities and large electrodes are vital for high space-time-yields. The experiments reported in literature also show that the product distribution depends on the electrolyte composition but no clear relations with the electrolyte properties were reported.^[35,36] Despite the high Faraday efficiencies, the oxidation of anhydrous methanol has not been investigated further. In-depth research is required to evaluate a potential industrial application of the electrochemical conversion of anhydrous methanol to formaldehyde.

In this work, the electrochemical oxidation of anhydrous methanol is investigated with respect to feasibility and scalability. To enable accurate potential measurements, a suitable reference electrode is developed. The reference electrode is used to test transi-

tion metals as electrode materials for the oxidation of anhydrous methanol to formaldehyde. Promising materials are studied in a scaled up flow cell and the influence of different reaction parameters, such as flow rate and temperature, are investigated. A systematic in-depth study of the electrolyte composition is conducted to evaluate the influence of basicity, conductivity and viscosity on the anhydrous methanol oxidation. For all those investigations, the Faraday efficiency and the specific energy consumption are the key evaluation parameters. To give insight into the occurring reaction mechanism, *in-situ* surface species on the electrode are analyzed.

2 State of the art

This chapter introduces the electrochemical fundamentals (section 2.1) and the possibilities and limitations of electrosynthesis in an anhydrous reaction environment (section 2.2). Thermal and electrochemical synthesis routes for aqueous and non-aqueous formaldehyde are discussed (section 2.3) and an overview about electrochemical engineering is provided (section 2.4).

2.1 Electrochemical fundamentals

Electrochemistry correlates electrical charge with chemical change. The fundamental relationships between charge, mass, and valence are described by Faraday’s two laws of electrolysis.^[38] Both laws are often summarized and relate the charge Q to the number of transferred electrons z , the number of involved atoms/molecules n and the Faraday constant F (Equation 2.1).^[39]

$$Q = znF \quad (2.1)$$

Faraday’s law describes all electrons involved in the occurring reaction. If only the desired reaction occurs, a Faraday efficiency (ϕ) of 100 % (Equation 2.2) is achieved.^[40]

$$\phi = \frac{\text{charge consumed in reaction of interest}}{\text{total charge passed}} \cdot 100 \% = \frac{n_{\text{exp}}}{n_{\text{theo}}} \cdot 100 \% \quad (2.2)$$

However, there are several possible causes that lower the Faraday efficiency of a reaction. Side products can be formed via alternative reaction pathways or subsequent reaction of the desired product. These subsequent reactions can be further oxidation or reduction occurring on the working electrode (WE) to form additional products. Alternatively, recombination of the product species can occur due to cross-over. The recombination is the reduction of an initially oxidized species back to the starting species or vice versa. Thus, charge is consumed during the reaction but no product

can be detected as the starting species is reformed. It is also possible that electrons are used up in the corrosion of the electrode or non-Faradaic processes, such as electrode oxidation. Therefore, it is important to determine the amount of charge that goes into the desired product compared to the total charge.

To correlate the amount of product formed with the required energy, one can calculate the specific energy consumption E_s using previously discussed quantities and the stoichiometric factor ν_p .

$$E_s = \frac{E_{\text{cell}}It}{n_p} = \frac{E_{\text{cell}}zF}{\phi\nu_p} \quad (2.3)$$

Another important parameter in electrochemical measurements is the resistance R_u of the electrolyte solution. The electrolyte resistance dampens the recorded voltage/current signal according to Ohm's law (Equation 2.4).^[41]

$$E_{\text{ion}} = R_u I \quad (2.4)$$

2.2 Electrosynthesis

Electrosynthesis is the process of applying an electric potential as the driving force for non-spontaneous reactions.^[42] The first electrochemical organic synthesis goes back to 1834 when Michael Faraday described the formation of hydrocarbons during the electrolysis of potassium acetate.^[38] Hermann Kolbe investigated the underlying mechanism in 1848–49,^[43,44] and the Kolbe electrolysis is still a widely used reaction.^[42,45,46] Using electricity as a driving force, electrosynthesis has several potential benefits compared to conventional thermally-driven reactions. First, an electrified process can be directly fed with electricity from sustainable sources. Second, the electricity enables new reaction pathways that often allow mild reaction conditions and a high functional group tolerance.^[47,48] Third, the redox reaction is carried out by electric current without the need for more traditional stoichiometric redox agents. This leads to an intrinsic scalability and sustainability of electrochemical processes.^[45,47,48] These advantages became more important in recent years as the fight against global warming progressed leading to a renaissance of the electrosynthesis.^[42,45,46]

Industrially, electrosynthesis is used for a variety of reactions (e.g., hydrogenation, methoxylation, reduction of carboxylic acids and nitro groups).^[49,50] Many electrochemical processes are conducted on a relatively small scale ($\leq 200 \text{ t a}^{-1}$) as they are part of a specialized product chain. One of the largest organic electrochemical synthe-

sis processes is the hydrodimerization of acrylonitrile to adiponitrile, a precursor for the nylon synthesis with $\geq 2 \times 10^5 \text{ t a}^{-1}$.^[49]

2.2.1 Non-aqueous electrolytes

An efficient electrosynthesis requires a suitable electrolyte for a fast ion transfer between the electrodes. Historically, electrochemistry started with the voltaic pile in 1800, thus it relied on aqueous electrolytes.^[51] Still, the majority of literature focuses on aqueous electrochemistry as water has several desired solvent properties.^[52] Non-aqueous electrolytes are diverse, yet little literature is available describing their properties on a fundamental level.^[52–54] They first attracted interest in the 1930s and onwards, and the research interest grew after 1950 along with increased interest in electrosynthesis.^[42,54] Non-aqueous electrolytes require an appropriate conductive medium, which can be an organic (e.g., acetonitrile, methanol) or an inorganic solvent (e.g., liquid ammonia, sulfur dioxide), ionic liquids, and supercritical fluids.^[52] The conducting medium does not have to be liquid as it can also be a conducting polymer and a solid.^[53] In this work, liquid organic solvents with different supporting electrolytes (conducting salts) were investigated. The dissolved supporting electrolyte within the solvent is referred to as the electrolyte. In the case of conducting polymers, solids and ionic liquids, the term electrolyte describes the whole ion-conductive medium.

Comparison of aqueous and non-aqueous electrolytes

When choosing a suitable electrolyte for a specific reaction, one must be aware of its advantages and limitations. Water is often used as a solvent as it is cheap, abundant and non-toxic. Aqueous solutions often have a high ion mobility and, thus, a high ionic conductivity, and the high heat capacity of water allows an efficient heat transfer.^[55] But aqueous electrolytes are also limited by the physical and chemical properties of water. Water is a polar solvent in which many non-polar substances are not soluble. Water is also a protic solvent that reacts violently with all alkali and some alkaline earth metals. These intrinsic properties restrict the available substrate and electrode choices. The electrochemical stability of water is restricted to a thermodynamic potential window of 0–1.23 V vs standard hydrogen electrode (SHE) with the hydrogen evolution reaction (HER) occurring below and the oxygen evolution reaction above

the potential window.^[55] Aqueous electrolytes can only operate within the temperature range between freezing and boiling points of water. Despite its limitations, water is the preferred solvent whenever possible primarily due to its high conductivity.

Non-aqueous electrolytes are versatile as they can be chosen based on the reaction requirements. Solvents can be e.g., polar aprotic like dimethyl sulfoxide (DMSO)^[56] and dimethylformamide (DMF)^[57] or different solvents can be mixed to achieve the desired properties.^[52,54,58] Reactions that require high potentials can be carried out in e.g., acetonitrile, which has a stability window of -3 to +3 V vs ferrocene (fc).^[59] Electrochemical reactions can also be conducted at higher temperatures of up to 1000 °C in solid oxide fuel cells.^[60] Yet, non-aqueous electrolytes also come with a couple of challenges, including lower conductivities than aqueous electrolytes. They are more expensive than water and tend to require more complex purification after use. Some solvents, such as methanol and benzene, which are flammable and toxic, provide additional safety hazards.^[52,53] Because of varying properties, non-aqueous electrolytes offer greater versatility in their approach but need to be tailored to the desired reaction system.

Classification of solvents

Electrochemical reactions are heavily influenced by the used solvent. Therefore, solvents are sorted into different categories based on their physical (such as boiling point, dipole moment, relative permittivity) and chemical properties (acidity, basicity, donor/acceptor characteristics for protons, electrons and hydrogen bonds).^[52] For non-aqueous electrolytes, often used criteria are the relative permittivity and the acid-base properties as both describe the solvent effects on the solutes, in this case the supporting electrolyte.^[52,57,61,62]

The permittivity of the solvent has major influence on solute-solute interactions, dissolution and dissociation of the supporting electrolyte. A fully dissociated supporting electrolyte provides many mobile ions that can transport charge through the electrolyte, which is a sign for a highly conductive electrolyte. Permittivity describes the polarizability of a substance in an electric field and it is often given as the relative permittivity ϵ_r , in a ratio with the vacuum permittivity ϵ_0 . A highly polarizable solvent can stabilize the charge of the dissociated salt lowering the Gibbs free energy of solvation ($\Delta_{\text{solv}}G^0$). The polar solvent can also shield identical charges from each other by surrounding them or complexation.^[52] The electrostatic contribution to $\Delta_{\text{solv}}G^0$ can

be estimated with the Born equation (Equation 2.5), which correlates $\Delta_{\text{solv}}G^0$ and the required work to transfer an ion from vacuum ϵ_0 to a solvent ϵ_r requiring the charge of the ion z_i , the elemental charge e , the Avogadro constant N_A and the radius of the molecule r_i .^[63] Other contributions to $\Delta_{\text{solv}}G^0$ include electron donor/acceptor interactions and interactions of the hard and soft acids and bases (HSAB) concept.^[52]

$$\Delta_{\text{solv}}G^0 = -\frac{z_i^2 e^2 N_A}{8\pi\epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r}\right) \quad (2.5)$$

Another important characteristic of solvent-solute interactions is the dipole moment of the solvent. Intrinsic solvent dipoles can also stabilize solute ions via coordination. Most solvents have an intrinsic permanent dipole moment (μ) due to unevenly shared electron density between neighboring atoms. Solvents with high μ (≥ 2.5 D) are called dipolar solvents while those with low dipole moments are called nonpolar solvents.^[52] However, these purely physical properties are insufficient to properly correlate the solute-solute and solute-solvent interactions. These interactions are also heavily influenced by the acid-base properties of the solvent.

The most commonly used parameter for acid-base properties is the pH value that describes the H^+ -ion activity in diluted aqueous solution. The "p" denotes the negative decimal logarithm of the given quantity. The more general acid dissociation constant K_a is given for an example reaction of an acid with water to their conjugated acid and base pairing $\text{HA} + \text{H}_2\text{O} \longrightarrow \text{A}^- + \text{H}_3\text{O}^+$ in Equation 2.6.^[63] Water dissociates spontaneously to H_3O^+ and OH^- due to its amphiprotic properties, which means that it can react as an acid as well as a base.^[64] Thus, the acid-base properties of aqueous solutions exist within the boundaries of the auto-dissociation value of water $\text{p}K_w$ (Equation 2.7).^[63]

$$K_a = \frac{a(\text{H}_3\text{O}^+)a(\text{A}^-)}{a(\text{HA})} \quad (2.6)$$

$$\text{p}K_w = 14 = \text{p}K_a + \text{p}K_b \quad (2.7)$$

Both, the acid and base constant, are based on the Brønsted-Lowry definition that acids are proton donors and bases are proton acceptors.^[63] For non-aqueous electrolytes, the definition for acids is extended to the ability to accept electrons and for bases the ability to donate electrons.^[52] Different methods were developed to determine the acidity of non-aqueous solvents.^[65–68] One classification that combines the relative permittivity and the acid-base properties was introduced by Brønsted and, later, refined by Davis and Kolthoff.^[57,61,62] The classification by Kolthoff is shown in Table 2.1. Solvents are divided into two categories, the amphiprotic and aprotic solvents.^[57] Amphiprotic

solvents (SH) undergo autoprotolysis with the reaction $2\text{SH} \rightleftharpoons \text{SH}_2^+ + \text{S}^-$.^[52] The reference for an amphiprotic solvent with a similar acidity and basicity to water is called *neutral*. Solvents that are stronger acids are *protogenic* and stronger bases are *protophilic*. Each subtype is split into solvents with high relative permittivity ($\epsilon_r \geq 20$) and low permittivity.^[57]

Aprotic solvents do not have a hydrogen atom connected to an electronegative atom, and thus, they have weak proton-donating and hydrogen bond-donating abilities. The basicity of aprotic solvents varies with strong bases being *protophilic* and weak bases being *protophobic*.^[57] Solvents with low permittivities, small dipole moments and weak acidic and basic properties are called inert solvents.^[52,57]

DMSO is listed in both amphiprotic and aprotic solvents. In the literature, DMSO is often described as an aprotic solvent.^[52] However, DMSO can undergo autoprotolysis as it has a moderately stable dimethyl-sulfonium anion ($\text{CH}_3\text{SOCH}_2^-$)^[52,57] In this work, methanol-based electrolytes are investigated, which is in the same amphiprotic neutral category as water. While they have similar acid-base properties, they deviate strongly in the relative permittivity with $\epsilon_r = 33$ for methanol and $\epsilon_r = 78$ for water.^[52]

Effect of solvent properties on chemical reactions

The dominating solvent properties that influence chemical reactions are the permittivity and acid-base properties. A difference in a chemical reaction in two solvents that differ by $\epsilon_r \geq 20$ can be usually attributed to the difference in relative permittivity. If both solvents have a similar permittivity, the acid-base properties determine the influence on the occurring reaction. A summary of the acid-base properties of solvents and their influence on chemical reactions is shown in Table 2.2.^[52]

The solvent effects are explained with the example of a weakly acidic solvent, e.g., acetic acid. A solvent with weak acidity is a weak hydrogen (bond) donor and dissociates only weakly to its conjugated base. Thus, the dissociated anions are highly reactive, and such solvents possess only poor proton-donating properties. This can interfere with the ion transport or reactivity of an electrochemical reaction. A weakly acidic solvent is a weak electron acceptor, which makes the solvent difficult to reduce. This behavior can stabilize strong reducing agents, and some substances that are irreducible in water due to its stability window can be reduced.^[52]

Table 2.1: Kolthoff's classification of organic solvents.^[57]

Amphiprotic solvents				
Subtype	ϵ_r ^a	Acidity ^b	Basicity ^b	Examples
Neutral	+	+	+	water, methanol, ethylene glycol
	–	+	+	<i>tert</i> -butanol, cyclohexanol
Protogenic	+	++	±	H ₂ SO ₄ , HF, HCOOH
	–	++	±	acetic acid
Protophilic	+	±	++	<i>N</i> -methylacetamide, DMSO, formamide, tetra-methylurea
	–	±	++	ethylenediamine, tetramethylguanidine
Aprotic solvents				
Subtype	ϵ_r	Acidity	Basicity	Examples
Dipolar protophilic	+	– (±)	+	DMF, DMSO
	–	–	++ (+)	pyridine, dioxane, tetrahydrofuran, ether
Dipolar	+	–±	–	acetonitrile, ketones, acetone, nitromethane
Protophobic	–	–	–	methyl isobutyl ketone, methyl ethyl ketone
Inert	–	–	–	aliphatic hydrocarbons, CCl ₄ , benzene

^a + indicates $\epsilon_r \geq 20$, – indicates $\epsilon_r < 20$ ^b referenced to water: ++ much stronger, + comparable, ± moderately weaker, – much weaker**Table 2.2:** Acid-base properties of solvents and the characteristics of reaction.^[52]

Weakly acidic solvents	Weakly basic solvents
Solvation to small anions is difficult.	Solvation to small cations is difficult.
Proton donation from solvent is difficult.	Proton acceptance by solvent is difficult.
Reduction of solvent is difficult.	Oxidation of solvent is difficult.

2.2.2 Non-aqueous reference electrodes

Electrochemical reactions can be investigated with direct current (DC) and alternating current (AC) experiments. Common DC experiments include cyclic voltammetry (CV), chronoamperometry (CA) and chronopotentiometry (CP). Electrochemical impedance spectroscopy (EIS) is a widely used AC experiment. To selectively investigate the working electrode (WE), at which the reaction of interest occurs, a suitable reference electrode (RE) is required that has three main quality parameters. The reaction on the counter electrode (CE) is often investigated separately.

The first quality parameter of a suitable RE is a stable, ideally non-polarizable potential. In an ideal non-polarizable electrode, the potential remains fixed when a current flows through it.^[69] Thus, the potential of the real reference electrode should only shift minimally with different currents. The potential of the RE should not only be reliable, it should also be stable over time. Small deviations can be accepted but should be less than ± 5 mV.^[70] In aqueous electrolytes, the standard hydrogen electrode (SHE) is the defined reference point of 0 V at all temperatures.^[71] The SHE is specified as the hydrogen evolution reaction (HER) on Pt in an acidic electrolyte (pH value = 0, e.g. 1 mol L⁻¹ HCl) and H₂ purging with a pressure of 10⁵ Pa.^[72] However, the SHE is impractical to use in most electrochemical cells, and thus, secondary REs are often utilized.^[69,71] Secondary REs need a defined and stable potential vs SHE and they usually consist of two solids in contact with each other, such as Ag/AgCl or Hg/Hg₂Cl₂ in KCl.^[69]

Using the SHE in a non-aqueous electrolyte provides a different potential than it does in an aqueous environment. The obtained HER potential depends on the chosen solvent as a more strongly solvated H⁺ leads to more negative potential.^[52] In addition, the potential of the HER becomes unreliable as the Pt electrode is highly sensitive to poisoning, especially by organic species.^[73] Instead of measuring potentials vs SHE, the International Union of Pure and Applied Chemistry (IUPAC) recommends the use of one of two reference redox systems: ferrocene/ferrocenium (fc/fc⁺) or *bis*(biphenyl)chromium(I)/*bis*(biphenyl)chromium(0).^[74] These redox systems also allow potential comparison between different solvents as they provide almost constant potentials regardless of the solvent.^[74]

The second quality parameter of a good RE is a low impedance to avoid potential distortions when measuring the WE potential. Thus, the RE impedance should be as low as possible.^[69,75–77] In non-ideal REs, impedances are mainly caused by the electrolyte and the isolation junction, e.g., an electrode frit.^[52,77] The electrolyte only provides

real (ohmic) resistance Z' to the total RE impedance Z . The isolation junction functions as a capacitor that contributes Z' as well as imaginary reactance jZ'' .^[69,77] The real and the imaginary parts of the impedance can be plotted in cartesian coordinates (Figure 2.1) and the impedance can be calculated depending on the phase angle ϕ_a (Equation 2.8).^[69,78]

$$Z = Z' + jZ'' = |Z| \cos \phi_a + j|Z| \sin \phi_a \quad (2.8)$$

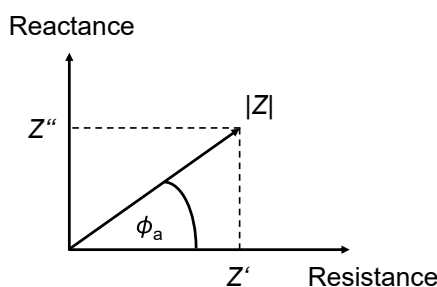


Figure 2.1: Impedance Z plotted as a planar vector in the complex plane between resistance Z' and reactance Z'' . Adapted from Barsoukov *et al.*^[78]

Reactances, whether they are capacitive or inductive, only occur when an AC is applied. Therefore, the impedance simplifies to the resistance in DC measurements. In a system only containing resistances, the current and potential are in phase (Figure 2.2 a)). A varied potential is immediately matched by the appropriate current response. The RE resistance causes a shift to higher potentials for anodic currents and lower potentials for cathodic currents (see Ohm's law, Equation 2.4). These shifts become more pronounced at higher currents.^[79]

In AC measurements, the reactance cannot be neglected and the overall RE impedance has to be taken into account. Current and potential are shifted by the phase angle ϕ_a . In the case of an ideal capacitor, the current precedes the potential signal by $-\pi/2$ or 90° (Figure 2.2 b)).^[69] This phase shift is used to measure the impedance of an RE via EIS in which a potential or current is applied, and ϕ_a of the other quantity is measured. The phase angle should be close to 0° at high frequencies as this indicates a system with small reactances.^[80] A negative ϕ_a is expected for REs due to the capacitive behavior of the junction.^[69]

There are additional setup influences on fast AC measurements. Any resistance R followed by a capacitor C can act as a RC low pass filter, which occurs in, e.g., the RE^[77] but also at the WE and CE due to the formation of an electrochemical double layer on the electrode surface.^[69]

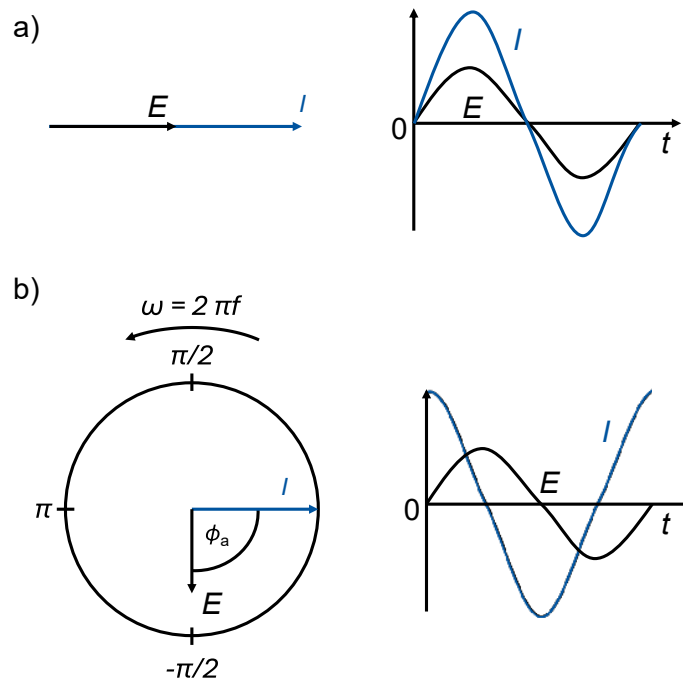


Figure 2.2: Phase shift and current-voltage response for a) an ohmic resistance and b) an ideal capacitor. Adapted from Bard *et al.*^[69]

A RC low pass filter passes low frequency signals unimpeded but it severely limits the signal output above a cutoff frequency f_c . To explain how a RC low pass filter works, Figure 2.3 shows the RC element of the RE and the capacitor in the reference input of the potentiostat.^[70,81] For easier explanation, the capacitive contributions in the RE are neglected so the RE impedance simplifies to the RE resistance R_{RE} . An unknown potential difference (voltage) occurs between the WE and the RE (U_{WE-RE}) that potentiostat measures over the capacitor C ($U_{measured}$). Behind the capacitor, the voltage drops to 0 V as the system is connected to the ground. The smallest applicable frequency is $f = 0$ Hz, which is an applied DC. For a DC, no current can flow through the capacitor. According to Ohm's law, there is no voltage drop over R_{RE} so all of the potential has to fall off over C and $U_{WE-RE} = U_{measured}$. For $f \rightarrow \infty$, the reactance of C $Z_c \rightarrow 0$ V, and a current can flow through the system. When a current flows, the potential drops over the R_{RE} according to Ohm's law (Equation 2.4), so $U_{measured}$ becomes damped compared to U_{WE-RE} .

The RE's impedance affects both DC and AC measurements, yet, the latter are more influenced by high impedances. For aqueous AC measurements, well-known electrochemical manufacturers recommend that REs impedances above 1 k Ω should be avoided and impedances above 5 k Ω cause unreliable measurements.^[80]

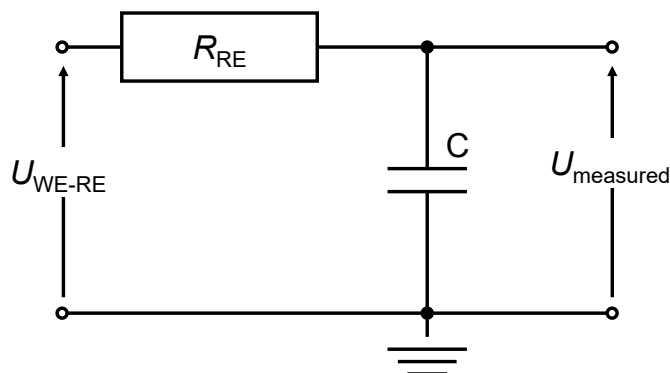


Figure 2.3: Schematic illustration of the RC low pass filter consisting of the RE resistance R_{RE} and the potentiostat capacitator C . Adapted from Gamry technical^[81] and application notes.^[70]

The third quality parameter of a suitable RE is the use of proper RE solvents. Electrochemical reactions can occur in aqueous or non-aqueous media, which provide vastly different reaction environments. Yet, aqueous REs are sometimes used in these non-aqueous reaction environments.^[82–87] Thus, the RE has a different solvent than the electrochemical cell inducing liquid junction potentials (LJPs).^[74] At the junction, several phenomena contribute to the formation of LJPs (Figure 2.4).

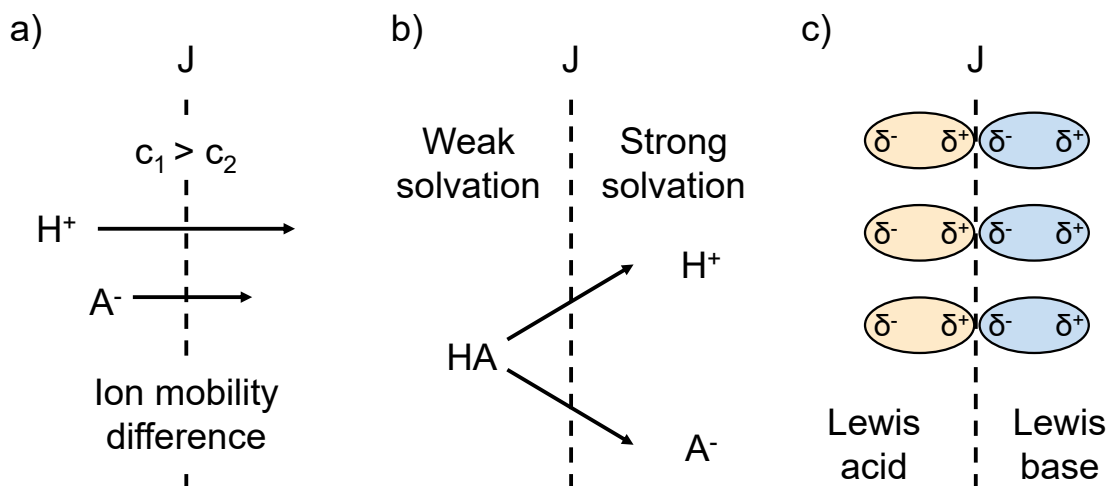


Figure 2.4: Schematic overview about contributors for LJPs between electrolyte solutions caused by a) a supporting electrolyte concentrations gradient with different anionic and cationic mobilities, b) different solvation energies, c) solvent-solvent interactions at the junction J. Adapted from Izutzu *et al.*^[52]

When two electrolyte solutions with the same supporting electrolyte but different concentrations meet, a LJP forms due to the different ion mobilities of the anion and cation causing a charge separation at the junction. At a junction of different solvents,

the supporting electrolyte is easier dissolved in one of them, which causes a charge imbalance across the junction. If the different solvents also have different Lewis acidities, the solvent molecules can organize according to their respective charges.^[52]

LJPs are detrimental for electrochemical measurements as they can provoke an unknown potential shift of up to 200 mV across different solvents.^[52,74,88] In the case of different solvents, there is the additional risk of interdiffusion through the porous membrane, which can contaminate the cell electrolyte or cause frit clogging due to different solubilities.^[71,89,90] The frit clogging introduces an unknown and changing resistance to the RE, which can lead to irreproducible measurements.

An alternative to aqueous REs are Ag/Ag⁺-based REs^[91–93], Ag/Ag-cryptate,^[52] Pt/I₃[−] + I[−]^[94] or a pseudo-reference electrode, e.g., a Ag wire^[95]. Ag/AgCl REs are also reported for use in non-aqueous media, yet, no experimental or quality parameters are provided.^[71] The Ag/Ag⁺ RE can be filled with the same electrolyte as is used in the electrochemical cell to avoid solvent-solvent LJPs. Thus, only the concentration gradient LJP of the used Ag salt contributes.^[74] While LJPs can be minimize with Ag/Ag⁺ REs, they prove unstable for extended periods of time.^[71] The RE potential and its stability depends on the solubility and stability of the Ag⁺ ion in the presence of the electrolyte. Any impurity can change the RE’s potential but often they provide reproducible potentials within ± 5 mV.^[52,71] It is also important to report the concentration of the Ag salt and the supporting electrolyte that were used in the RE construction as both affect the RE’s half-wave potential.^[90] The half-wave potential $E_{1/2}$ is calculated with the CV peak potentials of the redox system measured during the oxidative (E_{ox}) and reductive (E_{red}) sweep (Equation 2.9).

$$E_{1/2} = \frac{E_{\text{ox}} + E_{\text{red}}}{2} \quad (2.9)$$

All of these effects need to be considered when choosing a suitable RE for the reaction system. A suitable RE needs a stable potential, has a low impedance and uses the same solvent as the cell to minimize LJPs. The RE needs to be checked regularly for potential drift, frit clogging or leakage. These quality parameters enable the selection of a RE that guarantees reliable and reproducible results.

2.3 Formaldehyde

Formaldehyde naturally occurs as a metabolic intermediate of plants and animals and was also detected in interstellar space.^[11,96] It was discovered by Alexander Butlerov in 1859 and it has been produced industrially since 1889.^[11] Since then, it has grown to be one of the most important platform chemicals with an annual production of 45.6×10^6 t.^[10] The applications for formaldehyde range from the production of polymers (such as polyoxymethylene ethers and resins (urea, melamine, phenol)) to a versatile C1-building block in organic synthesis and biology.^[11,97]

All currently used industrial formaldehyde processes are based on methanol. The possible oxidation pathways of methanol are shown in Figure 2.5.^[98,99] The green arrows indicate the pathways leading to formaldehyde and the black arrows the pathways to CO. Pathways of the full oxidation to CO₂ are marked with gray arrows, which requires additional oxygen that is supplied by water from the reaction environment. The actually occurring reaction pathway depends on the driving force (thermal or electrical), the used catalysts/electrodes and the reaction environment. These influences will be discussed in the corresponding chapters.

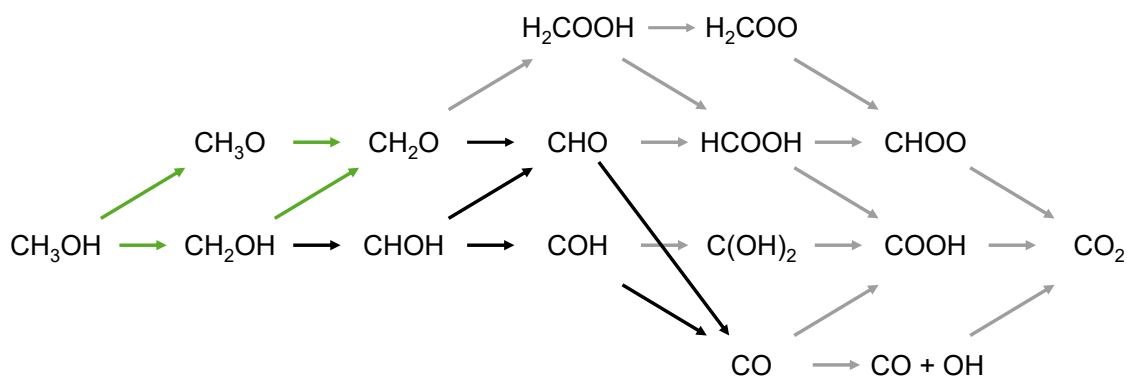
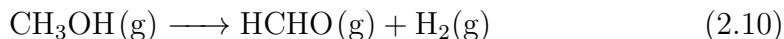


Figure 2.5: Schematic representations of the reaction pathways and intermediates of the methanol oxidation. Reaction pathways leading to formaldehyde are marked green, to CO black, to CO₂ in gray. Adapted from Ferrin *et al.*^[98]

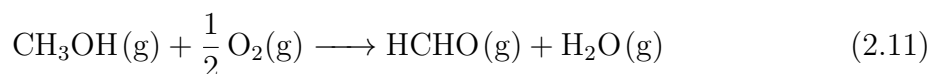
2.3.1 Conventional thermal synthesis

There are two main processes for the industrial formaldehyde synthesis, the Formox process and the Ag contact process with either full or partial conversion. The Formox process uses a FeMoO_x or VO_x catalyst and operates in a medium temperature range

of 250-400 °C with excess air, which results in a conversion of $\geq 98\%$. The Ag contact process employs Ag crystals and has a gas feed containing air, methanol and steam. The full conversion route ($\geq 97\%$) operates at 650-720 °C whereas the partial conversion ($\geq 77\%$) operates at 600-650 °C with a subsequent methanol recycling.^[11] The two main reaction pathways leading to formaldehyde have hydrogen (Equation 2.10) and water (Equation 2.11) as side products.^[11,100–103]



$$\Delta H = +84 \text{ kJ mol}^{-1}$$



$$\Delta H = -159 \text{ kJ mol}^{-1}$$

The Formox process runs exclusively via the oxidation reaction Equation 2.11, producing water as coupled product^[11,104] according to the Mars van Krevelen mechanism.^[105] Methanol is oxidized by lattice oxygen of the $\text{MoO}_3\text{--Fe}_2(\text{MoO}_4)_3$ catalyst and the vacancy is refilled by the feed-stream air.

In contrast to the Formox process, the Ag catalyst requires steam in its methanol-air feed to help the surface restructuring process and catalyst activation.^[106–108] Both methanol oxidation pathways (Equation 2.10 and Equation 2.11) occur with the dehydrogenation shown in Equation 2.10 being the dominant pathway.^[11,104,109] The Ag catalyst requires high temperatures and the presence of oxygen to be active.^[109] Under these reaction conditions, three different types of oxygen in or on the catalyst (O_α , O_β , O_γ) were observed (Figure 2.6). O_α is adsorbed on the surface^[109,110] as Ag_2O .^[111,112] O_β is oxygen that diffuses into the octahedral holes of the Ag structure.^[113] Both, O_α and O_β , react with methanol via Equation 2.11.^[109,110] O_γ is a tightly bound oxygen species that is only formed at elevated temperatures ($\geq 620^\circ\text{C}$), which goes along with an additional surface restructuring.^[107,114,115] The nature of that oxygen is not conclusively determined. There are indicators for oxygen diffusion in the structure that coordinates to six Ag atoms symbolized as $\text{Ag}=\text{O}$.^[115] Others results suggest that oxygen substitutes Ag in its lattice structure forming a metastable Ag sub-oxide.^[110,116,117] In both cases, O_γ carries a negative charge, which makes it a strong Lewis-base.^[109,115,116] These basic properties selectively catalyze the dehydrogenation reaction of methanol (Equation 2.10).^[109,115]

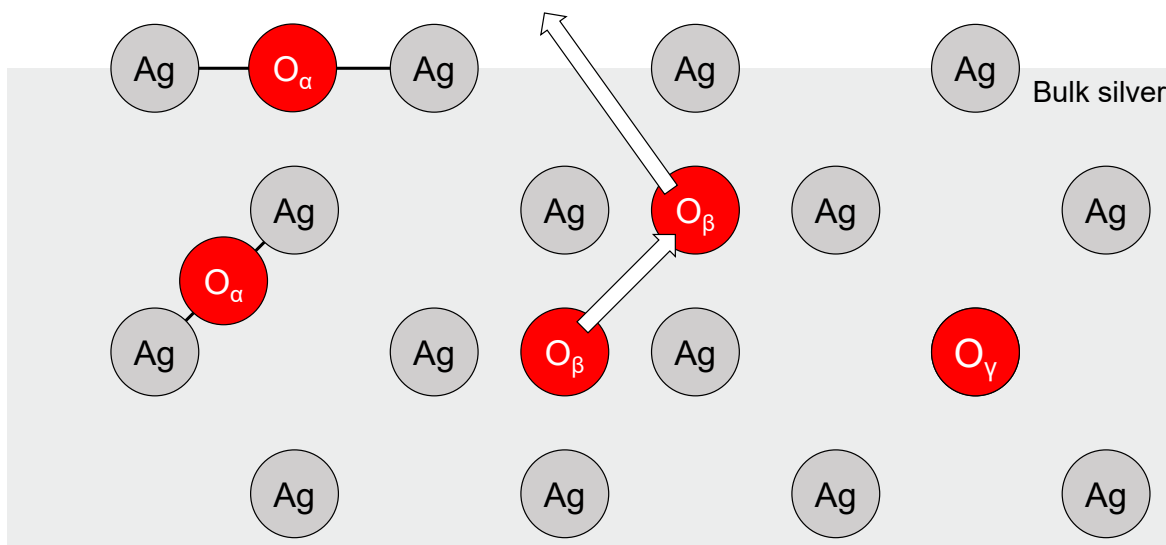


Figure 2.6: Schematic representation of the oxygen species (O_α , O_β , and O_γ) in and on the catalyst. Note that O_γ can also be formed by coordination with six Ag atoms as $\text{Ag}=\text{O}$,^[115] which is not shown in this figure. Adapted from the Master thesis of Florian Schwarz.^[118]

Because of the occurring reactions and required reaction conditions, the Ag as well as the Formox process produce aqueous formaldehyde solutions with a maximum of 55 wt% formaldehyde.^[119] However, many applications demand anhydrous formaldehyde, e.g., polyoxymethylen dimethyl ethers, which necessitates complex and energy-demanding water removal due to the formation of a water-formaldehyde azeotrope.^[120–122] The energy demand for a separation by distillation of a 50:50 formaldehyde-water mixture was estimated around 1 MJ kg^{-1} with the software COMSOL by William Graf von Westarp (AVT.FVT). Industrially, formaldehyde is dried via paraformaldehyde, which is obtained by concentrating aqueous formaldehyde solutions under vacuum conditions.^[11] Thus, there is industrial interest in anhydrous formaldehyde without requiring water removal.

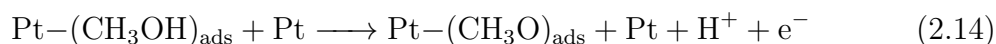
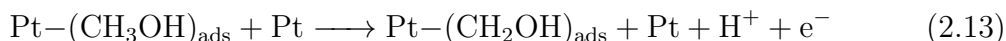
2.3.2 Alternative aqueous synthesis routes

Instead of a thermally induced reaction, methanol can also be oxidized electrochemically at milder reaction conditions, e.g., as a side reaction in direct methanol fuel cells (DMFCs). While DMFCs can be operated at high temperature with solid oxide electrolytes^[123], many operate in a temperature range of 30–100 °C and rely on Nafion(-type) membranes.^[124] The presented results rely on studies using a liquid aqueous methanol solution without the use of an additional membrane. In DMFCs, the desired

reaction is the total oxidation of aqueous MeOH in presence of O_2 to CO_2 and H_2O . Formaldehyde only occurs as a side product and it was investigated how the reaction conditions influence its formation.^[29,31] For example, the formaldehyde formation depends on the pH value of the electrolyte with acidic media favoring formaldehyde compared to alkaline.^[33] Even though formaldehyde was an unwanted product in DMFCs, some investigations were made into the deliberate electrochemical conversion of aqueous methanol to formaldehyde. In 1989, Yamanaka *et al.* achieved a conversion rate to formaldehyde of $1.33 \mu\text{mol min}^{-1} \text{cm}^{-2}$ on a Pd_{black} electrode in a gaseous methanol-water-helium feed.^[10,27] Liu *et al.* used gaseous methanol and an acidic electrolyte and attained 75 % selectivity on polycrystalline Pt and a formation rate of $0.65 \mu\text{mol min}^{-1} \text{cm}^{-2}$. They also state that low-water content on the anode is favorable for the formaldehyde formation^[28] as it reduces the amount of possible side reactions.^[99] Batista *et al.* achieved 81 % selectivity to formaldehyde in 1.0 mol L^{-1} methanol and $0.5 \text{ mol L}^{-1} H_2SO_4$.^[125] The methanol oxidation to formaldehyde was also scaled up and tested in an electrochemical flow reactor (40 cm^2 electrodes) with a Faraday efficiency of 51 % after 4 h in 8.0 mol L^{-1} methanol and $0.5 \text{ mol L}^{-1} H_2SO_4$.^[32]

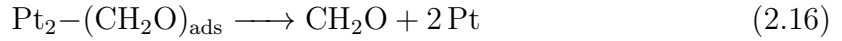
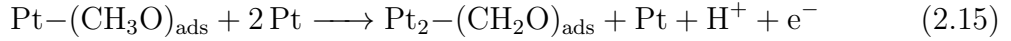
The reaction mechanism of methanol oxidation was mostly investigated as part of the methanol oxidation reaction (MOR) on Pt electrodes in DMFCs. There are two major reaction pathways for the total electrochemical oxidation of methanol to CO_2 : the direct mechanism for the total oxidation and the indirect mechanism, which goes via a CO-intermediate.^[126] The dominant reaction pathway depends, among other factors, on the Pt surface structure,^[127] the available Pt-sites,^[128] the solvent,^[129] the supporting electrolyte,^[125,128] and the pH value of the electrolyte.^[33] An overview of the possible pathways on Pt is provided in this chapter, a more detailed version can be found in Housmans *et al.*^[128] and Cohen *et al.*^[33]

The presented reaction mechanism occurs in an acidic electrolyte, e.g., H_2SO_4 or $HClO_4$.^[128] The MOR starts with methanol adsorption on the Pt surface (Equation 2.12)^[33] followed by the dehydrogenation via C–H (Equation 2.13) or O–H (Equation 2.14) bond cleavage.^[33,128,130]

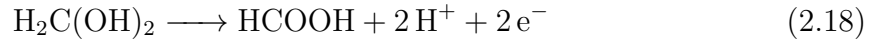
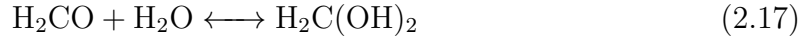


The indirect reaction mechanism to CO is favored after the C–H bond cleavage. After an initial O–H bond cleavage, the formation of soluble liquid products (formaldehyde

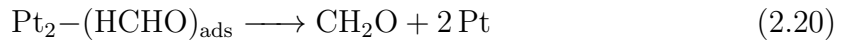
and formic acid) is more likely as the reaction always proceeds via formaldehyde.^[127] Both intermediates can then undergo a second dehydrogenation step. $\text{Pt}-(\text{CH}_3\text{O})_{\text{ads}}$ further reacts via a C–H bond cleavage (Equation 2.15) creating adsorbed formaldehyde on the Pt surface, which can then dissolve into solution (Equation 2.16).^[128] Cohen *et al.* report that formaldehyde is double bound on the Pt surface^[33] while Housmans *et al.* state that formaldehyde is only bound via the oxygen.^[128]



Housmans *et al.* were not able to confirm, whether a direct subsequent oxidation of formaldehyde to CHO is possible. They suggest that desorbed formaldehyde spontaneously forms methanediol with surrounding water (Equation 2.17),^[131–133] which can then be oxidized to formic acid (Equation 2.18).^[128] In contrast, Cohen *et al.* reported that the methanediol pathway is unlikely and that adsorbed formaldehyde is directly oxidized to CHO (Equation 2.21).^[33]

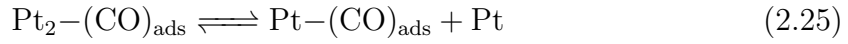
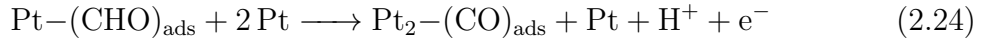


If a C–H bond cleavage is followed by a O–H cleavage (Equation 2.19), several subsequent reaction steps are possible. According to Cohen *et al.*, formaldehyde can desorb into solution (Equation 2.20) or it can be further oxidized to a CHO surface species as long as a vacant Pt-site is available (Equation 2.21). It can also react with an adsorbed hydroxy species on the Pt surface to formic acid (Equation 2.22).^[33] Housmans *et al.* state that $\text{Pt}_2-(\text{CHOH})_{\text{ads}}$ exclusively undergoes subsequent oxidation to a CHO species via Equation 2.21.^[128]

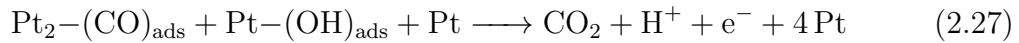
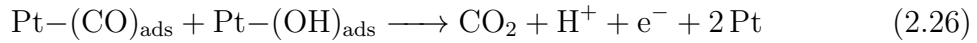


Housmans *et al.* and Cohen *et al.* agree that the direct methanol oxidation pathway proceeds to CO after the CHO intermediate.^[33,128] The last dehydrogenation of CHO can be supported by either OH^- (Equation 2.23) or two vacant Pt sites (Equation 2.24). The OH^- pathway results in linearly bound CO while the second pathway

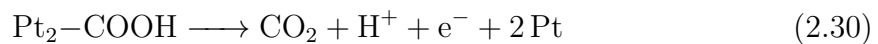
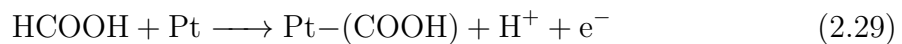
produces bridged bound CO.^[33] Both CO species can be transformed into each other via Equation 2.25.^[10]



Because of the strong Pt–CO interactions, the formation of CO is often considered to be a reversible poisoning. Thus, CO is unlikely to desorb but it is oxidized to CO₂ by a nearby Pt–OH species with Equation 2.26 for linearly bound CO and Equation 2.27 for bridged CO.^[33]



Housmans *et al.* and Cohen *et al.* report that formic acid can form during the MOR (Equation 2.18 and Equation 2.22), which is present in the electrolyte solution.^[33,128] Formic can adsorb on the surface with both oxygens (Equation 2.28)^[128] or with just one (Equation 2.29).^[33] The adsorption of the second oxygen is only described by Cohen *et al.* as part of the subsequent oxidation to CO₂.^[33] Both agree on the proceeding oxidation step (Equation 2.30).^[33,128]



As part of the DMFC research, not only the total methanol oxidation to CO₂ was investigated, but also reaction conditions that favor the partial oxidation products formaldehyde and formic acid. Thus, several favorable reaction conditions for the formation of formaldehyde were found. Formaldehyde (and formic acid) are formed in the beginning of the electrochemical reaction. With long reaction times and high formaldehyde concentrations, it becomes more likely that formaldehyde adsorbs to the electrode again and is oxidized further.^[26]

Another important factor is the Pt surface structure. According to Cao *et al.*, the O–H bond scission is favored on Pt(111) surfaces in H₂SO₄, after which the reaction always occurs via the formaldehyde intermediate. For Pt(100), the C–H bond cleavage was calculated to be the preferred pathway, but the O–H bond cleavage still occurs.^[127]

The Pt surface can also be oxidized under electrochemical conditions.^[134] The methanol oxidations on Pt starts at 0.5 V vs the reversible hydrogen electrode (RHE).^[125,135] At higher potentials ≥ 1.05 V vs RHE, Pt is oxidized to PtO₂,^[134] which is an electrode poison species for the methanol oxidation according to Li *et.al.*^[136] Other studies still showed an activity for PtO₂ for the methanol oxidation to CO₂^[135] while an even higher activity for PtO₂ was reported for the formaldehyde formation.^[32]

The surface environment is not only intrinsic to the electrode, but it is also influenced by the adsorbing species. In acidic DMFCs, H₂SO₄ is an often used supporting electrolyte with a higher formaldehyde selectivity compared to HClO₄. The sulfate anions strongly adsorb on the Pt electrode and partly poison the surface. Consequently, less Pt sites are vacant and available for further oxidation steps. The indirect methanol oxidation pathway via the C–H bond scission requires more free Pt sites, and is, thus, inhibited whereas the direct oxidation pathway is less affected.^[125,128] For the alkaline methanol oxidation, it was reported that a low NaOH concentration increases the formaldehyde production whereas a high concentration, and thus a better OH[−] availability, encourages further oxidation.^[31] It was also found that high initial methanol concentrations favor the formation of formaldehyde and formic acid.^[26,31] A high methanol concentration increases the amount of adsorbed methanol on the electrode surface and, thus, limits the amount of neighboring available adsorption sites that enable subsequent oxidation.

For the methanol oxidation to CO, four neighboring adsorption sites are required, which is only available on flat surfaces. On surface edges, only one or two hydrogen can be stripped from methanol leading to =CHOH species.^[137] While surface edges are beneficial in limiting the dehydrogenation sites, rough and porous surfaces facilitate further oxidation.^[26,135] On smooth Pt, formaldehyde and formic acid are the main products. On rough surfaces, the intermediates have a higher chance to contact the electrode again and get subsequently oxidizes.^[135]

An influence of available Pt sites was also reported for the formaldehyde formation on Pt/C, which depends on the particle size. On small and finely dispersed particles (1-3 nm), the adsorption sites have few available neighbors, which favors the formation of formaldehyde.^[138] On medium sized particles (4-10 nm), the particles have terraces and steps in close proximity to the reactive site, so formaldehyde can be oxidized further.^[10,138] On large particles (>10 nm), the formaldehyde formation increases again despite available Pt sites for further oxidation. Instead of subsequent oxidation, the desorption becomes favored as formaldehyde has a lower adsorption energy on larger Pt particles.^[138]

Besides the electrode material and supporting electrolyte, it was found that the mass transport influences the formaldehyde formation. In an rotating disc electrode setup, increasing amounts of formaldehyde were formed with increasing rotation rates.^[31] This indicates that a short contact time on the electrode favors the formaldehyde formation by avoiding subsequent oxidation.

Methanol can also be oxidized to formaldehyde via photocatalytic conversion. Mesa *et al.* achieved a Faraday efficiency of 96 % on α -Fe₂O₃ with formaldehyde as the only reaction product. However, they were only able to produce 35 μ mol in 47 min.^[139] Photocatalysis offers advantages such as mild reaction conditions and using sunlight as its sole energy source. Yet, it has several challenges to overcome to be applied in an industrial scale^[10] and, thus, is not discussed further in this work.

2.3.3 Anhydrous thermal synthesis

A dehydrogenation-based methanol oxidation starting from pure methanol does not require energy-intensive water removal unlike the conventional synthesis. It offers the additional benefit of hydrogen recycling (Equation 2.10) that can be used for energy storage or CO₂ recycling.

Because of the growing interest in anhydrous formaldehyde, several materials were investigated as thermal dehydrogenation catalysts. Early success was found with transition metal catalysts, such as Ag, Cu, Zn and In, at operation temperatures of 250-760 °C.^[10,140] A Ag/Cu catalyst converted 85 % of the methanol with a selectivity to formaldehyde of 92 % at 620 °C. This catalyst requires oxygen to be active and the activity in absence of oxygen is low.^[140] Oxygen is assumed to play a vital catalytic role in the selective dehydrogenation similar to the oxygen in industrially used Ag catalysts. Surface and sub-surface oxygen was detected and appeared to activate the material or be active itself.^[141,142] At high temperatures, the dehydrogenation reaction becomes the dominant pathway, but some oxidation to water still occurs. In some materials, oxygen was replaced with phosphorus. A silica-supported Cu catalyst containing phosphorus converted 57 % with 81 % selectivity while only 33 % were converted without phosphorus.^[140] The formaldehyde formation on a FeTi alloy was increased by the addition of 20 at.% Zn, which lowered the selectivity from 64 % to 50 %.^[143]

Additionally, Na-based catalysts were tested successfully as a homogeneous vapor and as a salt at elevated temperatures. Na₂CO₃ converted 14 % with a selectivity of 92 % at 623 °C. When the conversion was increased to 55 %, the selectivity drops to 84 %.

To balance this effect, it is possible to increase the selectivity by the addition of In. However, Na_2CO_3 catalysts always deactivate over several hours due to coking and sintering before a stable activity is achieved. Exchanging the cation to, e.g., potassium or caesium leads to a lower selectivity to formaldehyde.^[140]

Experiments with a Na vapor catalyst converted 95 % of the methanol to formaldehyde with a selectivity of over 83 % with CO as the major side product. At conversions lower than 20 %, a formaldehyde selectivity of 100 % was achieved.^[144] Here, elemental Na seems to be the active species. Experiments with gaseous NaOMe instead of Na vapor showed similar turnover numbers with comparable conversions and selectivities to formaldehyde. Ruf *et al.* propose the decomposition of NaOMe to elemental Na and a methoxide radical $\text{CH}_3\text{O}^\bullet$. Two methoxide radicals then decompose to two formaldehyde molecules and H_2 . Reactions using Na vapor catalyst still require suitable Na recovery methods as Na is carried out of the reactor with the product stream.^[121]

New catalytic materials for the selective dehydrogenation include $\text{SO}_4^{2-} - \text{Ce}_2(\text{MoO}_4)_3$ loaded on SiO_2 at 325 °C, which yielded 100 % conversion to formaldehyde for small scale experiments.^[145] Recently, a high formaldehyde selectivity of 77 % at 550 °C was reported for bulk $\beta\text{-Ga}_2\text{O}_3$, yet, the catalyst deactivated rapidly after 2 min.^[146] The stability of the material was improved by using silica, which enabled oxidative regeneration. The dehydrogenation properties of the material was attributed to the presence of Brønsted acidic sites at the interphase between GaO_x species and SiO_2 .^[147] A more detailed overview about the thermal routes can be found in reviews by Su *et al.*^[140], Usachev *et al.*^[148] and Deitermann *et al.*^[10].

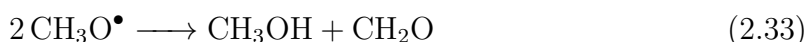
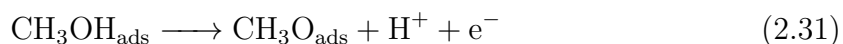
2.3.4 Anhydrous electrochemical synthesis

Methanol can also be dehydrogenated electrochemically. This allows a water-free synthesis and also the direct use of electricity without further conversion to thermal-energy, which is an additional benefit for the electrification of the overall process. However, only a few fundamental studies were carried out on the electrochemical dehydrogenation of anhydrous methanol.^[34–37,149]

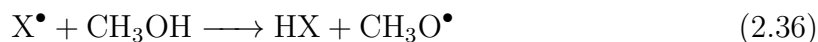
First results were obtained by Sasaki *et al.* in 1964/65., who investigated low concentrated NaOMe, NaOH, NaClO_4 , NH_4F , NH_4Cl , NH_4Br and NH_4I as supporting electrolytes in anhydrous methanol.^[34,149] NaOMe was the most active one for the methanol conversion to formaldehyde with 75 % Faraday efficiency, which was also confirmed by Sundholm in 1971.^[34,35] NH_4F performed similarly to NaOMe, and the

Faraday efficiency decreased with the anion exchange from $F > Cl > Br > I$.^[34] The supporting electrolyte NBu_4F produced dimethoxymethane as the main product.^[35] No formaldehyde was found when sodium phenoxide ($NaOC_6H_5$) was used as the supporting electrolyte.^[36] A variety of transition metals (Pt, Ni, Ag, Fe, Cu, Ti, Hg) were tested as electrodes for the methanol dehydrogenation to formaldehyde. Among the tested metals, only Pt was found to be active for the anodic oxidation of methanol.^[36] However, most of these literature reports suffer from incomplete experimental documentation.

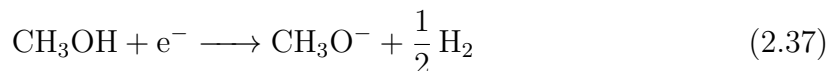
The occurring reaction mechanism of the oxidation of anhydrous methanol was also investigated. The influence of the NaOMe concentration on the peak currents of the respective redox wave was investigated by Iwakura *et al.*^[36] They determined a linear relation of the sodium methoxide concentration and the square root of the sweep rate, which indicates a reaction order of one for the methanol oxidation with respect to the methoxide anion.^[36] Belanger related the measured current with the sodium methoxide concentration with $\left(\frac{\partial \log I}{\partial \log c}\right)$ at two potentials. They confirmed a reaction order for methoxide of 0.9 for the lower potential and 0.82 for the higher potential.^[37] Sasaki *et al.* and Iwakura *et al.* observed gas evolution at both, the anode and the porous cell separator when an anodic current was applied to a NaOMe in MeOH electrolyte.^[36,149] The gas that formed at the separator contained more formaldehyde than the gas at the anode surface, and thus, the following reaction pathway was postulated:^[149]



Methanol adsorbs on the anode upon which the O–H bond is broken (Equation 2.31). The methoxide then desorbs into the solution as a radical (Equation 2.32). In the bulk solution, two methoxy radical can meet and disproportionate to methanol and formaldehyde (Equation 2.33). Another reaction pathway is the endothermic decomposition of the radical (Equation 2.34), whereas the disproportionation of two radicals is exothermic with 85 kcal mol^{-1} .^[149] The formation of methoxy radicals can also occur via the anion of the supporting electrolyte. The anion can pass an electron to the anode to form a radical (Equation 2.35), which can then be transferred to a methanol solvent molecule to create a methoxy radical in the bulk phase (Equation 2.36).^[34]



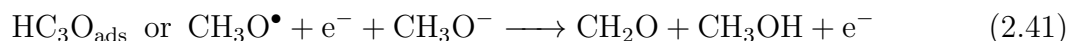
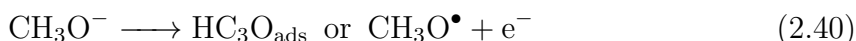
The active methoxide can also be formed at the cathode (Equation 2.37) when methanol is reduced. This was proposed by Iwakura *et al.*, as they measured the hydrogen evolution reaction with 100 % efficiency at the cathode.^[36]



To explain the formation of formaldehyde at the anode, Sasaki *et al.* suggested the oxidation of methanol to formaldehyde and adsorbed hydrogen (Equation 2.38). The hydrogen can then desorb (Equation 2.39) and move to the cathode to be reduced to hydrogen gas.^[34]



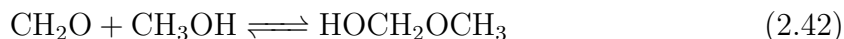
Belanger argues that the discharge reaction of the methoxide (Equation 2.40) is the rate determining step due to the reaction order of the species being nearly one. The discharged methoxy species can either adsorb on the surface or desorb as a radical. Both species can react with another methoxide to formaldehyde and methanol (Equation 2.41).^[37]



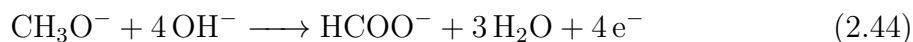
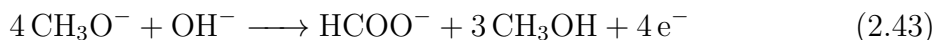
In contrast to the other studies, Belanger assumes that the reaction actually occurs on the electrode surface. An analysis of the methanol oxidation with a rotating disc electrode showed no definitive relationship between the rotation rate and the measured current. According to Belanger, this behavior indicates an activation-controlled reaction. However, a distinct difference between experiments with a standstill and a rotated electrode was observed. The current response dropped when the electrode was rotated, which suggests that an intermediate is transported away from the electrode surface.^[37]

The main product of the anhydrous methanol oxidation on Pt is formaldehyde, yet, several other products are possible. Formaldehyde spontaneously reacts to methanediol in the presence of methanol and water (Equation 2.17). Formaldehyde can also

react to methoxymethanol when it is bubbled through methanol (Equation 2.42).^[150] Formaldehyde can also be oxidized further to the final oxidation product CO (see Equation 2.24 in subsection 2.3.2), while the oxidation to CO₂ would require the addition of an external oxygen atom.^[34]



In the presence of OH⁻, a methoxide can react to formic acid (Equation 2.43 and Equation 2.44).^[37] Afterwards, further oxidation to CO₂ is possible (see Equation 2.28, Equation 2.22, Equation 2.30 in subsection 2.3.2).



Anhydrous formaldehyde can be synthesized electrochemically from methanol on Pt electrodes with sodium methoxide as the supporting electrolyte. As only a few studies were carried out to investigate the underlying reaction mechanism, it remains ambiguous how the reaction proceeds. Most of the proposed mechanisms can explain the observations made during the process and seem chemically intuitive but have little analytical support. Taking the investigations of the anhydrous thermal route and the aqueous electrochemical route into account, it is possible that the methoxide also plays a crucial role in the formaldehyde formation in the electrochemical oxidation of anhydrous methanol.

2.4 Electrochemical engineering

Few electrochemical syntheses have made it to large scale industrial production.^[49] Many more processes were developed for smaller quantities of more specialized products.^[49,151] Development of smaller processes require less investments and fine chemicals can be sold for a higher prize than bulk chemicals.

The research of an electrochemical reaction often starts on the laboratory scale with a focus on reaction selectivity and mechanistic understanding. Other factors, such as energy efficiency, process stability and economic feasibility, that are vital for in-

dustrial success are often neglected.^[151] Thus, additional research and adaption is required to transfer and scale up a successful laboratory-scale electrochemical organic synthesis.^[49] To understand how these different research priorities affect the "optimal" reaction conditions, the interplay between the electrolyte, the electrode and the cell design is described in more detail. For organic electrosynthesis, aqueous electrolytes often have insufficient solubility for non polar compounds, which is why organic solvents are used.^[151] Other differences between aqueous and non-aqueous electrolytes are discussed in more detail in subsection 2.2.1. Organic solvents often require a supporting electrolyte to increase the electrolyte conductivity, which can be an inorganic or organic salt. Organic supporting electrolytes are often toxic, volatile and flammable. In addition to their high production costs and difficulties in recycling, organic supporting electrolytes provide several challenges for large scale applications.^[151–153] It was recently found that the supporting electrolyte can also actively influence the reaction rates and selectivity of the electrochemical reaction. Blanco *et al.* and Hymel *et al.* report that an accumulation of ions in the electrochemical double layer can stabilize radical ion intermediates promoting the target reaction.^[154,155] As an alternative to organic solvents, ionic liquids or solid polymer electrolytes can be used. Ionic liquids have a high conductivity, thermal stability and recyclability. They are non-volatile and have a high solubility of organic compounds.^[156] However, they are often highly viscous, which limits the mass transport on the electrode, have high production costs and environmental concerns.^[151] Solid polymer electrolytes provide high energy efficiencies by reducing the electrode gap and ohmic resistances. But membrane contamination and stability remain major challenges in large scale application.^[151]

The next important aspect of an electrochemical setup is the electrode. The electrode can be an inert conductor or an electrocatalyst. The characteristics of the electrode are major influenced by the supporting electrolyte and the solvent.^[157] Changes to either of them can drastically change the reaction performance. Thus, both have to be investigated and optimized in tandem.^[151] In addition, the electrode stability is rarely investigated in the laboratory scale during short term measurements. Still, it is known that carbon electrodes show a decrease in performance due to the formation of a passivation layer on the surface^[158] and metal electrodes can corrode.^[159]

Both, the electrolyte and the electrode, come in contact in the electrochemical cell. In the laboratory, batch or single pass flow cells are often used. Conversely, in scaled-up processes, continuous flow electrolyzers with recirculating electrolytes are commonly used.^[151] These different modes of operation lead to different mass transport, heat transport and product removal.^[49,151] As the electrochemical reaction usually occurs

on the electrode-electrolyte interface, efficient mixing is vital for a high production rate. Industrial scale electrochemical plants also require easy handling for cleaning and maintenance.^[49]

The different research priorities can lead to vastly different recommended reaction conditions. For example, an electrochemical synthesis is highly selective and fully characterized using a diluted electrolyte on the laboratory scale. Due to the low supporting electrolyte concentration, the electrolyte conductivity is low. A scaled-up process would require much energy, which increases the product cost, and have high heat developments due to the ohmic resistance of the electrolyte. Instead of adjusting the reactor design to lower the heat development, a higher concentration of the supporting electrolyte is tested in the pilot plant to increase the electrolyte conductivity. However, this causes a vastly different reaction performance as the supporting electrolyte influences the reaction conditions on the electrode. As all of these parameters affect each other and the reaction performance, they need to be studied in tandem to enable a smooth scale-up from the laboratory to the industrial scale (Figure 2.7).^[49] To support the scale-up process, different modeling and empirical methods are developed by chemists and engineers to tackle this interdisciplinary challenge.^[151]

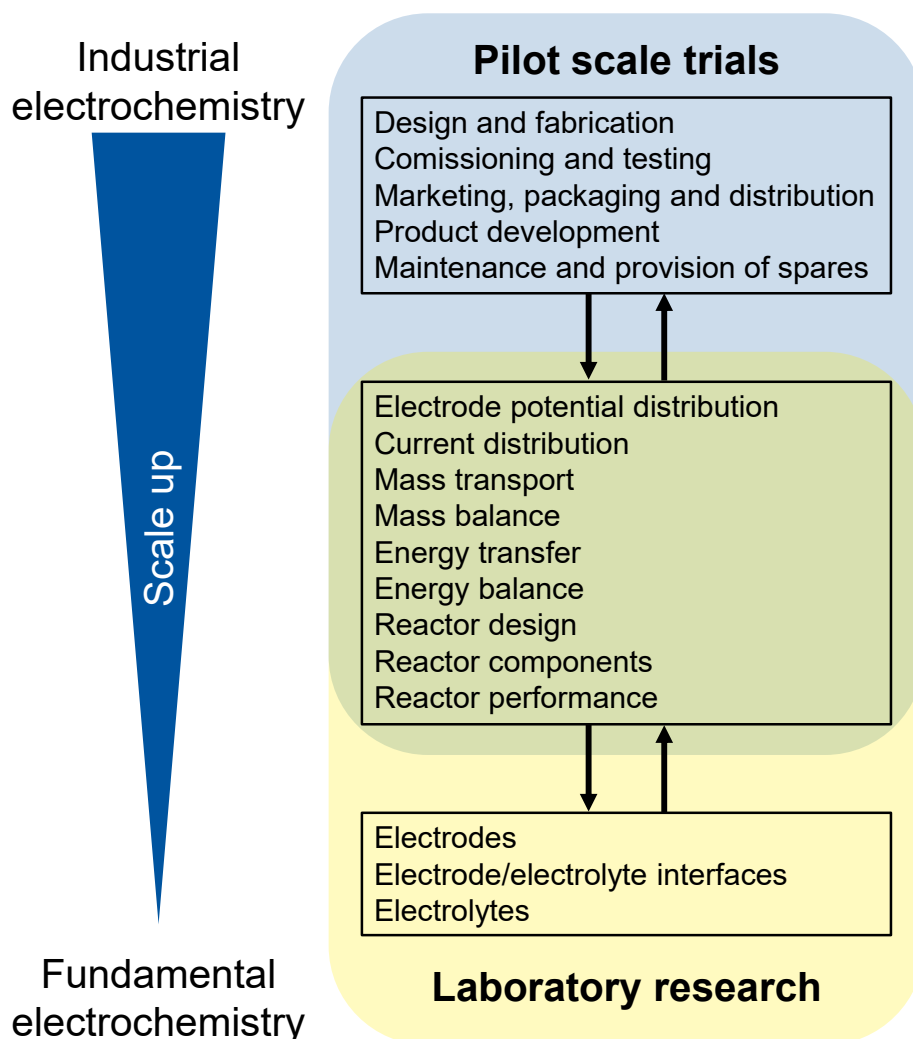


Figure 2.7: Overview of the scales and endeavors of electrochemical engineering. Adapted from Pletcher *et al.*.^[49]

3 Research questions & approach

Industrial processes need to adapt to renewable energy resources and reduce their greenhouse gas emissions, which can both be addressed via process electrification. One example for such an industrial process is the formaldehyde synthesis that up to now requires high temperatures. Its electrochemical synthesis allows ambient conditions and was proven successfully for the oxidation of aqueous methanol to formaldehyde. However, the reaction suffers from further formaldehyde oxidation, to, e.g., formic acid and CO_2 that lowers the overall efficiency of the formaldehyde conversion. The probability for side reactions can be reduced by using anhydrous methanol.

This work investigates in what way is the electrochemical anhydrous methanol oxidation to formaldehyde scalable for industrial application and how is it influenced by individual reaction parameters. To guarantee reliable measurements in an anhydrous reaction environment, a suitable RE has to be found. Ag/Ag^+ REs are often used REs in anhydrous reaction environments. Although they provide a stable RE potential, they lack long-term stability, and the influence of LJPs due to different Ag salts and supporting electrolytes is unknown. Ag/AgCl electrodes containing methanol and water were also reported for use in anhydrous media, yet no long-term stability is mentioned. Thus, the following questions arise:

1. How is the potential of Ag/Ag^+ REs influenced by LJPs?
2. Does a purely methanolic Ag/AgCl RE provide a reliable potential?
3. What are the application limits of Ag-based REs for DC and AC measurements in anhydrous methanol?

To address these questions, various Ag/Ag^+ REs containing different silver salts and supporting electrolytes are prepared and compared with regard to their potential. Since Ag/Ag^+ REs are known to be only short-term stable, methanolic Ag/AgCl REs are constructed analog to the aqueous Ag/AgCl REs. Their performance regarding a reliable potentials and long-term-stability is compared to the best performing Ag/Ag^+ RE

and a Ag wire pseudo RE. To estimate the application limits of the tested REs, their impedances are determined and the resulting impact on DC and AC measurements is calculated.

Once found, the suitable RE can be used to investigate the oxidation of anhydrous formaldehyde. The selective electrooxidation of anhydrous methanol to formaldehyde is reported in literature, yet most of these reports have incomplete experimental documentation. The applied experimental conditions were adapted based on existing literature and the methanol oxidation was explored as follows:

4. How does the electrode material and supporting electrolyte concentration influence the methanol oxidation to formaldehyde?

For this purpose, several anode materials are tested in a batch setup for their activity and selectivity to formaldehyde in different supporting electrolytes. These materials are compared for their stability and activity for the formaldehyde formation. To approach industrially more relevant conditions, promising materials are tested in a flow cell setup to allow inferences to following questions:

5. Can the methanol oxidation be scaled up with respect to electrode size and current density with electrolyte recirculation?
6. How is the scaled up setup affected by mass transport, electrode configuration and temperature?

To investigate scale-up effects, previously identified active materials are tested with larger electrode sizes and at elevated current densities in a flow cell setup. In addition, the scale-up introduces several new reaction parameters (e.g., flow rate, electrode gap and temperature) which effects on the formaldehyde formation is systematically studied. For a deeper understanding of the reaction performance under scaled up conditions, the electrolyte is investigated in more detail, and the following questions are considered:

7. How does the electrolyte composition affect the methanol oxidation?
8. What are the most influential supporting electrolyte properties?
9. How do the supporting electrolyte and applied current influence the reaction mechanism?

Thus, a systematic electrolyte variation and characterization is performed to gain insight into influential electrolyte properties and the reaction mechanism. The electrolyte effects on the reaction mechanism is also investigated by analyzing *in-situ* surface species. Understanding the interaction between the electrode and the electrolyte is vital for further scale-up as the electrolyte can modify the electrode surface, the reaction rate and the selectivity.

4 Materials and methods

All experiments in this work were conducted at ambient pressure. Unless otherwise noted, experiments were performed at room temperature (RT, 20-24 °C). The instruments used in this work are listed in Table A.1. All chemicals are listed in Table A.2. The chemicals were used without further purification. An overview about the used electrode materials is shown in Table A.3. The wire electrodes were cleaned with 1500 grit sand paper and rinsed with methanol before use. Metal plates and foils were used without prior cleaning. After the experiment, they were rinsed with methanol and air dried.

4.1 Reference electrodes

To find suitable REs for use in anhydrous methanol, different types of Ag based REs were investigated. The influence of different ions in Ag/Ag⁺ REs was analyzed in transparent and brown glass RE compartments. The brown glass filters UV light to minimize Ag⁺ precipitation. The transparent RE setups were purchased from ALS (RE-7N). They consist of Ag wires (44 mm length) and sample holders (6 mm diameter, 68 mm length, ion permeable porous glass tip). The brown glass RE compartment was provided by a glassblower with brown glass and a porous magnesium oxide tip. The Ag wire listed in Table A.3 was used. Both RE setups can be seen in Figure 4.1. The transparent electrode vials were also used for the construction of methanol based Ag/AgCl REs. The impedance and the stability over time was measured for the Ag/AgCl REs and it was compared to a Ag/Ag⁺ with minimized LJPs and a Ag wire.



Figure 4.1: Reference electrode compartments used in this work. The commercially available one used for the comparison of Ag-based REs (left) and the darkened glass vial to inhibit the Ag^+ precipitation for the ion influence study (right). Picture taken from the Bachelor thesis of Anne Liang.^[160]

4.1.1 Ion influence investigation in Ag/Ag^+ reference electrodes

To analyze the influence of different silver and electrolyte ions on the RE potential, several Ag/Ag^+ REs were constructed. The RE vials were filled with methanolic solutions containing one of two Ag salts (AgClO_4 , AgNO_3 ; 0.01 mol L^{-1}) and one of three supporting electrolytes (LiClO_4 , NaClO_4 , TBAP; 0.1 mol L^{-1}). REs with transparent vials were prepared twice and the brown glass REs were prepared five times each.

To measure the influence of the different ions on the LJPs present in the RE, the half-wave potential $E_{1/2}$ of the ferrocene/ferrocenium (fc/fc^+) redox couple was measured. These experiments were carried out with a Gamry 1010 E potentiostat. All REs were freshly prepared before each measurement. A two electrode setup was used in an H-cell setup with a Pt wire CE. The built RE was used as the WE. The open circuit potential (OCP) was measured for 150 s to give the electrodes time to equilibrate with the solution. The electrolyte consisted of 0.1 mol L^{-1} LiClO_4 or NaClO_4 and 5 mmol L^{-1} fc. 10 cycles were measured with a scan rate of 100 mV s^{-1} between 0.15 V and -0.55 V (Figure 4.2), as the initial CV curves were sometimes distorted $E_{1/2}$ was calculated with the peak potentials according to with Equation 2.9 (subsection 2.2.2).

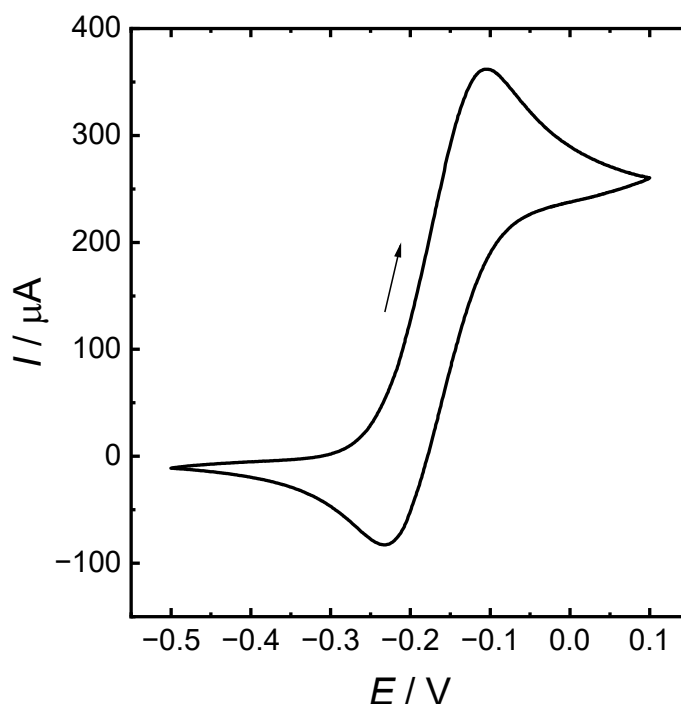


Figure 4.2: CV of an Ag/Ag^+ RE in a transparent compartment filled with 0.01 mol L^{-1} AgClO_4 and 0.1 mol L^{-1} LiClO_4 . The CV was measured with a scan rate of 100 mV s^{-1} in an H-cell containing $150 \text{ mL } 0.1 \text{ mol L}^{-1}$ LiClO_4 and 5 mmol L^{-1} fc in methanol.

4.1.2 Characterization of alternative Ag-based reference electrodes

After analyzing the influence of different Ag salts and supporting electrolyte ions on the Ag/Ag^+ LJP, its stability over time was measured. As Ag/Ag^+ REs are known to be only short term stable, two different methanolic Ag/AgCl REs were constructed as potentially more stable REs. Additionally, a Ag wire was prepared as a pseudo RE. For the construction of the Ag/AgCl and Ag/Ag^+ -REs, the RE setups supplied by ALS were used. For the pseudo reference electrode (RE 7), a pure Ag wire was used (Table A.3). After cleaning with sand paper, all Ag wires were dipped into 0.1 mol L^{-1} HNO_3 for 30 s and rinsed twice with ultra-pure water. All electrochemical measurements were carried out with a Gamry Reference 3000 potentiostat in a beaker cell setup with no additional separators. Two REs were prepared for each type of Ag/AgCl and Ag/Ag^+ to test the reproducibility, while for the Ag wire only one experiment was prepared. The different REs were prepared according to the following instructions:

Ag/AgCl after Brossia *et al.*: Brossia *et al.* reported a methanol-based Ag/AgCl RE that contained $0.66 \text{ mol L}^{-1} \text{ H}_2\text{O}$.^[161] The chloridization was carried out in a two-electrode beaker cell setup with a Pt wire CE. The wires were chloridized in $1 \text{ mol L}^{-1} \text{ HCl}$ at 0.4 mA cm^{-2} for 2 h. The chloridized wires were stored in pure methanol for 4 days. Afterwards, they were stored in $0.1 \text{ mol L}^{-1} \text{ LiCl}$ in methanol with the addition of $0.66 \text{ mol L}^{-1} \text{ H}_2\text{O}$. Two REs were prepared following this recipe and they are referred to as RE 1 and RE 2.

Ag/AgCl in pure methanol: Ag/AgCl REs were prepared according to Smith *et al.* as described in the Handbook of Electrochemistry.^[162] The chloridization was carried out in a two-electrode beaker cell setup with a Pt wire CE. The chloridization occurred in $1 \text{ mol L}^{-1} \text{ HCl}$ at 0.4 mA cm^{-2} for 30 min and the Ag/AgCl wire was stored in ultra-pure H_2O for 4 days. Afterwards, the REs were repeatedly rinsed with methanol and stored in $0.1 \text{ mol L}^{-1} \text{ LiCl}$ in methanol. These two reference electrodes are referred to as RE 3 and RE 4.

Ag/Ag⁺: The Ag wires were cleaned as previously mentioned and the glass compartments were filled with a methanolic solution of $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$ and $0.01 \text{ mol L}^{-1} \text{ AgClO}_4$. These two reference electrodes are referred to as RE 5 and RE 6.

Ag wire: The Ag wire was cleaned with sandpaper and rinsed with methanol before use. It is referenced as RE 7.

4.1.3 Stability and impedance measurements of anhydrous silver reference electrodes

To investigate the performance of the different Ag-based REs, CVs were measured to determine the long-term RE stability with regard to the fc/fc^+ redox couple. In addition, EIS measurements were performed to measure the REs impedances. All experiments were carried out with a Gamry 3000 potentiostat. A three-electrode glass beaker setup was used with a Pt wire WE and a glassy carbon rod CE. Each CV (background and fc) and EIS experiment started with 60 s OCP measurement.

Stability measurements: To investigate the potential stability of the different REs over time, $E_{1/2}$ of the fc/fc^+ redox couple was measured over a span of multiple days. A background CV scan was measured to verify that no methanol oxidation occurs in the potential window and to clean the electrode surfaces. The background was measured in 20 mL methanol with $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$ at scan rates 50 mV s^{-1} , 100 mV s^{-1} and 200 mV s^{-1} for 5 cycles each. A concentrated fc solution containing 0.025 mol L^{-1} in

0.1 mol L⁻¹ LiClO₄ was prepared, and 5 mL were added to the electrode setup, resulting in an electrolyte solution containing 5 mmol L⁻¹ fc and 0.1 mol L⁻¹ LiClO₄. 5 CV cycles were measured with different potential windows for the different electrodes: RE 1,2,3,4 from 0.1 V to 0.75 V, RE 5,6 from -0.5 V to 0.1 V and RE 7 from -0.1 V to 0.45 V. The peak potentials of the 5th CV cycle were used to calculate $E_{1/2}$ as described previously.

Electrochemical impedance measurements: To analyze the impedances of the different REs, electrochemical impedance spectroscopy (EIS) was performed. For the EIS measurements, the same glass beaker was used but in a two electrode configuration. The investigated RE was connected as the WE and a glassy carbon rod was used as CE. EIS was performed in a range of 5 kHz to 100 Hz with an applied potential of 5 mV (root mean squared) vs OCP. RE 1-4 were analyzed in 0.1 mol L⁻¹ LiCl in methanol and RE 5-7 in 0.1 mol L⁻¹ LiClO₄ in methanol. Different supporting electrolytes were chosen for the measuring cell electrolytes to minimize LJPs with the REs.

4.2 Electrochemical measurements and evaluation

Two different setups were used to investigate the methanol oxidation reaction (MOR). A batch H-cell setup was used without external mass transport. This setup was used to investigate the influence of several electrode materials and the electrolyte concentration. The second setup was a scaled-up flow cell with a recirculating electrolyte that was used to investigate the MOR under more industrial-near reaction conditions. The flow cell specifications are described in subsection 4.2.2. Unless noted otherwise, the experiments were conducted at RT.

4.2.1 H-cell

Initial studies were carried out in an H-cell setup (Figure 4.3), made from glass with a total volume of 200 mL. No separator between the half cells was used. The electrochemical measurements were carried out with a Gamry 1010 E potentiostat. A three electrode setup was used in the H-cell with the WE and the anhydrous Ag/AgCl RE (RE 5,6) being placed one side and the CE in the other one. The potential of the RE was measured vs the fc/c⁺ redox couple to verify its potential as described previously (subsection 4.1.3). The surface area of the WE wire was around 0.7 cm², which was calculated based on the length that it was immersed in the electrolyte.

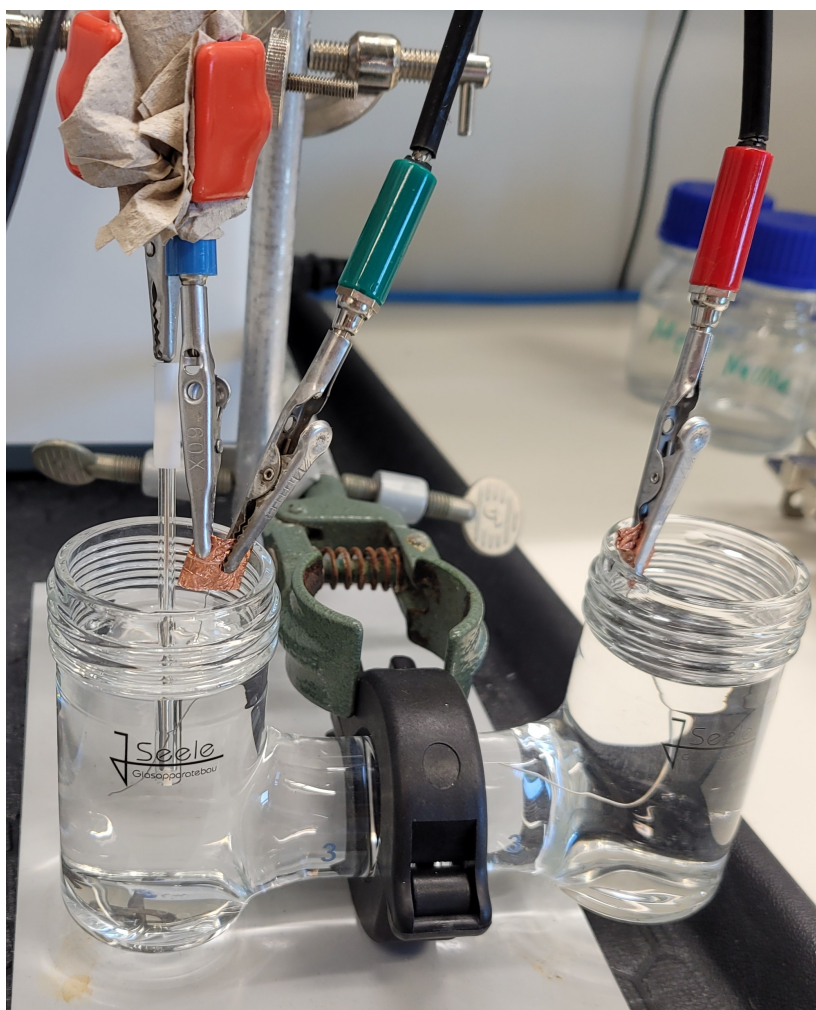


Figure 4.3: Picture of the used H-cell setup.

Material variation: For the material variation, a glassy carbon rod CE was used. The H-cell was filled with 150 mL electrolyte, which consisted of 0.1 mol L^{-1} NaOMe, 0.1 mol L^{-1} NaClO₄ or 1.0 mol L^{-1} NaOMe in methanol. One exception is the Ag wire that was measured in LiClO₄ instead of NaClO₄. 10 CV cycles were measured with a scan rate of 100 mV s^{-1} in the range of -0.5 - 2.5 V vs fc.

CAs were measured for 2 h in 0.1 mol L^{-1} NaOMe at the peak potentials of the CVs in the same electrolyte: Pt at 0.67 V , 1.30 V , 2.4 V ; Cu at 0.90 V ; Ni at 1.12 V , 1.40 V , 2.50 V ; Ag at 0.88 V , 2.4 V ; Au at 0.69 V , 1.12 V , 2.50 V vs fc.

Electrolyte concentration: To investigate the influence of the NaOMe concentration, higher concentrated electrolyte solutions were measured. For these experiments, a three electrode setup was used with a Pt wire as WE and CE and an anhydrous Ag/AgCl RE. Since the performance in 0.1 mol L^{-1} NaOMe was already known, only the increased electrolyte concentrations were measured. Two electrolyte solutions (175 mL)

were prepared containing 0.5 mol L^{-1} and 1.0 mol L^{-1} NaOMe in methanol. After an initial OCP for 60 s, a CA was conducted by applying 2.4 V vs fc for 2 h. These experiments were only performed once.

4.2.2 Flow cell

The MOR of anhydrous methanol was also investigated in a scaled up flow cell. Compared to the H-cell, this setup has larger electrode surfaces and a continuous mass transport due to flow conditions. Because several reaction and setup parameters were varied, a description of the experimental framework is given that stayed constant across all measurements. Afterwards, the standard reaction conditions are defined. The varied reaction parameters are described in separate paragraphs below.

Experimental framework: All experiments were carried out with a two electrode setup in a flex-E-cell flow cell by fxc engineering GmbH. The electrodes were parallel and the thickness of the electrode gap was adjusted by layering 1 mm thick santopren gaskets (Figure 4.4). The electrodes were connected to the cell via Cu-tape strips going through gasket cuts. A 3D-printed turbulence promoter (Formlabs) was enclosed in the gasket layers on the anode side to improve mass transport (Figure 4.5). No separator was used. The cell was tightened with 4 screws and 10 Nm pressure on each with a torque wrench. All experiments were carried out with a Gamry 3000 potentiostat. The potentiostat was connected to the WE via the working and working sense cell leads. The CE is connected via the counter and counter sense leads. The white cell lead was connected to the black floating ground cell lead. The setup is shown in Figure 4.6.

Experimental standard conditions: The cell gaskets determined the electrode gap as well as the available surface area of the electrode. The anolyte can catholyte flow channels each consisted of four gasket layers creating a 8 mm electrode gap. The surface area of the Pt foil anode was limited to 12 cm^2 and the Pt/Ti cathode (CE) limited to 25 cm^2 were used. The actual electrode sizes are listed in Table A.3.

After assembly, the cell was flushed with 60 mL methanol to test for tightness. During the cell flushing, the electrolyte solution was prepared. The flushing methanol was removed from the cell by switching the flow direction of the peristaltic pump. The cell was then flushed with 40 mL of the prepared electrolyte to minimize concentration changes caused by remaining methanol in the cell. The flushing electrolyte was removed and 40 mL electrolyte were prepared in a glass beaker for the electrochemical measurement.

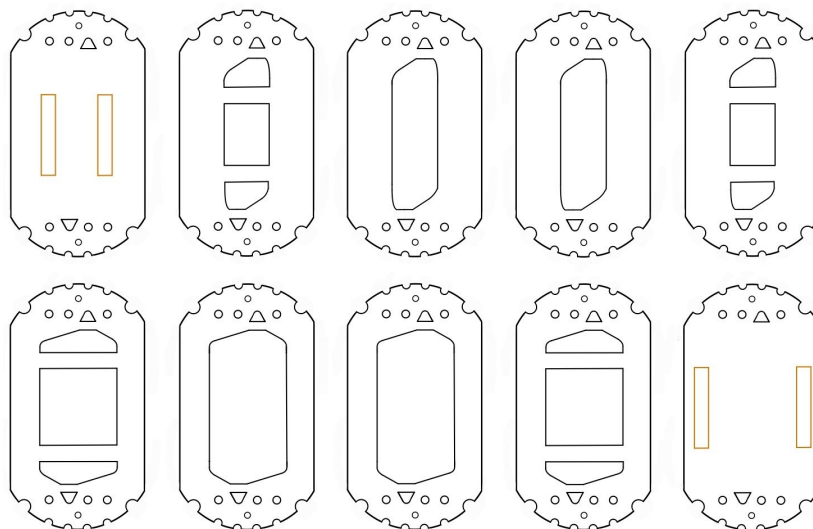


Figure 4.4: Gasket layers in the flow cell setup. Each layer was cut from 1 mm thick santoprene. The brown rectangles represent Cu tape used to electrically connect the electrode with the current collector. The top gaskets are for the anode side, the bottom row make up the cathode side. Picture taken from the Master thesis of Elizabeth Larenz.^[163]

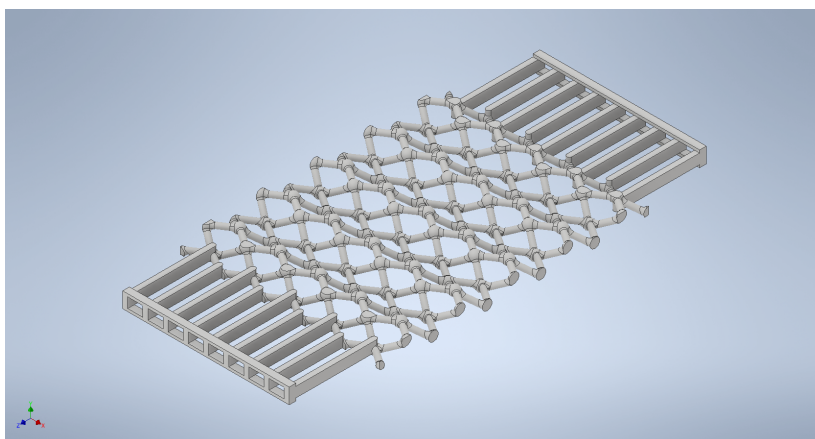


Figure 4.5: 3D printed turbulence promoter for the anode side.

A blank sample was taken from the remaining prepared electrolyte solution. The sampling process is described in more detail in subsection 4.2.3. The electrochemical measurements started with 60 s OCP. Afterwards, a 30 min CP measurement was performed during which the electrolyte was recirculated with a flow rate of 100 mL min^{-1} . After the electrochemical experiment, the electrolyte was pumped out of the flow cell, collected and the volume was measured and a sample was taken. The cell was twice rinsed with methanol and once with new electrolyte between consecutive experiments. Unless otherwise noted, these conditions were used. In the following paragraphs, the experimental and procedure variations are described.

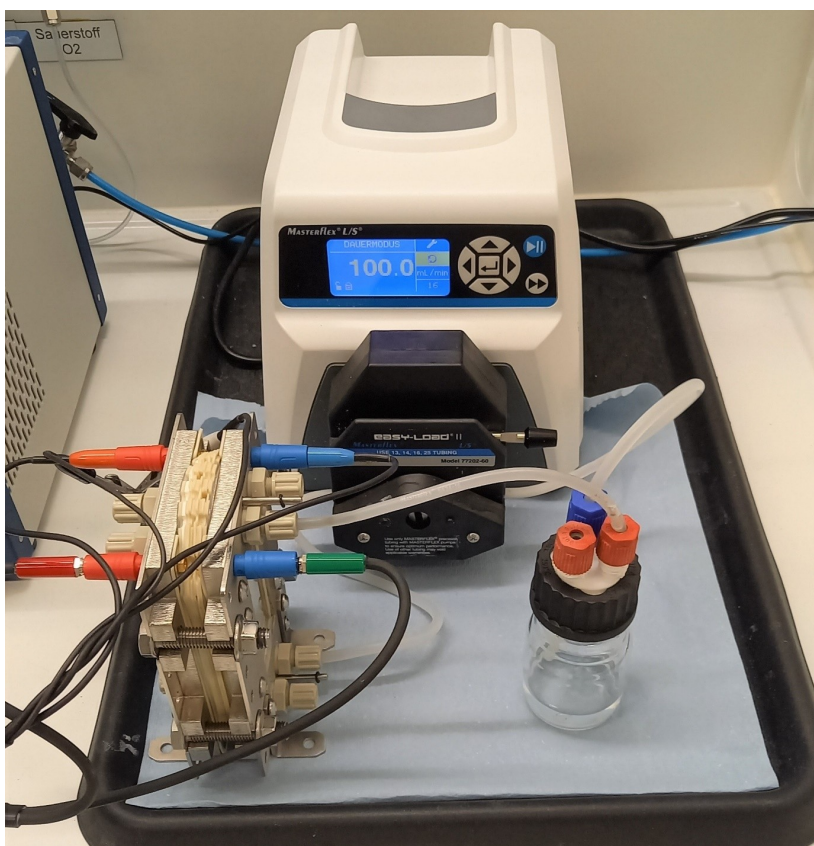


Figure 4.6: Picture of the used flow cell setup that was taken from the Master thesis of Elizabeth Larenz.^[163]

Anode material variation: The following materials were tested on the anode side: Pt foil, Ni foil, Au foil, Pt/Ti (12 cm²), Pt/Ti (25 cm²) carbon GDE, Pt/C GDE. In this study, 0.1 mol L⁻¹ NaOMe was used. The applied current density was increased from 10-100 mA cm⁻² in 10 mA cm⁻² steps.

Flow rate variation: The flow rates were varied for each 0.1 mol L⁻¹ and 1.0 mol L⁻¹ NaOMe. At 3 mA cm⁻², the flow rates 10, 50, 100 and 150 mL min⁻¹ were measured. At 100 mA cm⁻², the flow rates 10, 50, 100, 150, 200 and 300 mL min⁻¹ were measured.

Electrode gap variation: The electrode gap was decreased to 4 mm by removing the cathode gasket layers. It was increased to 12 mm by adding one set of additional cathodic flow frames. CPs were measured in 0.1 mol L⁻¹ and 1.0 mol L⁻¹ NaOMe at 10 mA cm⁻² and 100 mA cm⁻².

Temperature influence: The electrolyte temperature was adjusted by placing the electrolyte reservoir in hot water bath of 40 °C or an ice bath. The electrolyte temperature was measured inside the glass beaker with an analog thermometer.

Electrolyte screening: CPs were measured in both 0.1 mol L^{-1} and 1.0 mol L^{-1} at 10 mA cm^{-2} for each electrolyte: NaOtBu, LiOMe, NaOMe LiClO₄, NaClO₄, KClO₄, H₂SO₄, and KOH. KClO₄ was only measured in $> 0.1 \text{ mol L}^{-1}$ because of low solubility. Additional supporting electrolytes (CH₃COOH, H₂PO₄, KH₂PO₄, K₂HPO₄, Na₂SO₄) could not be tested due to insolubility or insufficient conductivity.

Electrolyte variation: The supporting electrolytes NaOMe, LiOMe, NaClO₄, and LiClO₄ were investigated in more detail. The applied current density was increased from $10\text{--}100 \text{ mA cm}^{-2}$ in 10 mA cm^{-2} steps in 0.1 mol L^{-1} and 1.0 mol L^{-1} for these 4 electrolytes. For KOH, one additional measurement for each concentration was carried out at 100 mA cm^{-2} .

Electrolyte mixtures: Electrolytes containing NaOMe and NaClO₄ were prepared. For that purpose, 0.1 mol L^{-1} , 0.5 mol L^{-1} and 1.0 mol L^{-1} NaClO₄ were added to each, a 0.1 mol L^{-1} and a 1.0 mol L^{-1} NaOMe solution. The mixed electrolytes were investigated at 10 mA cm^{-2} and 100 mA cm^{-2} .

Formaldehyde concentration: To investigate the influence of the formaldehyde concentration, single pass experiments were performed. To ease experimental practicability, the flow rate was decreased to 10 mL min^{-1} and the electrolyte volume was increased to 400 mL . These experiments were performed with 0.1 mol L^{-1} and 1.0 mol L^{-1} NaOMe. An initial CP single pass was performed at 10 mA cm^{-2} for 30 min . After the CP, the electrolyte was collected and its total volume was measured. Then, an electrolyte sample was taken to measure the amount of products formed during the pass. The electrolyte volume was refilled to a total volume of 400 mL with methanol. To prepare the next CP single pass experiment, an additional electrolyte sample was taken to account for the products in the electrolyte from the previous pass. Then, another CP pass was performed until a total reaction time of 4 h (8 passes) was achieved. Afterwards, the electrolyte flow was switched from single pass to recirculation and another 16 h CP was measured. The same series of CP measurements was performed with a current density of 100 mA cm^{-2} . One set of passes was also measured with a flow rate of 100 mL min^{-1} . To allow experiments with these high flow rates, the following experimental adjustments were made: 2000 mL of 0.1 mol L^{-1} NaOMe were prepared and the time of each CP pass was reduced to 15 min . To keep the total reaction time constant 4 h , the number of passes was increased to 16 . A current density of 100 mA cm^{-2} was applied. Otherwise, the same procedure was used as previously described.

Potential-dependent reaction mechanism: The potential dependency of the reaction was investigated by measuring CPs in 0.1 mol L^{-1} and 1.0 mol L^{-1} NaOMe at 4 , 10 , and 100 mA cm^{-2} .

4.2.3 Sample extraction and handling

To analyze the products of the MOR, electrolyte samples were taken before and after the CP measurements. 1 mL of the electrolyte solution was transferred to a glass screw top vial with a glass pipette. The vial was closed with a screw cap containing a PTFE/red silicone septum. The samples were stored in the fridge at 4 °C until they were measured to minimize potential chemical side reactions.

It was also investigated whether the MOR products were stable with regards to the electrolyte pH value. Therefore, a standard flow cell experiment was run with 0.1 mol L⁻¹ NaOMe at 100 mA cm⁻² for 30 min. Afterwards, three samples with 10 mL each were taken from the electrolyte. Sample 1 was taken for reference and not changed. The alkalinity of sample 2 was increased to 1.0 mol L⁻¹ by the addition of solid NaOMe. The alkalinity of sample 3 was also increased to 1.0 mol L⁻¹ by the addition of concentrated 5.4 mol L⁻¹ NaOMe (30 wt.%) solution. This increased the volume of sample C to 12 mL. Afterwards, all three samples were stored in the fridge at 4 °C for 3 d before analysis.

4.2.4 Evaluation of the data

The conducted experiments were analyzed with regard to their Faraday efficiency and the specific energy consumption E_s . The following paragraphs describe on how these analysis parameter were obtained.

Calculation of the Faraday efficiency: To calculate the Faraday efficiency according to Equation 2.2, the amounts of produced and theoretically possible substance are required. To determine the amount of products formed during the reaction, the experimental samples were analyzed via high performance liquid chromatography (HPLC) for the concentrations of formaldehyde and formic acid. The produced amount was determined with the measured concentrations according to Equation 4.1

$$c_{\text{prod}} = c_{\text{fin}} - c_{\text{init}} \quad (4.1)$$

The HPLC results were given in mg L⁻¹. To convert the concentration of the produced substance to the amount n , the molar mass M and the electrolyte volume after the experiment V are used according to Equation 4.2.

$$n_{\text{prod}} = \frac{cV}{M} \quad (4.2)$$

The theoretical amount of possible formed product was calculated with Faraday's law (Equation 4.3, see also section 2.1). The number of transferred electrons z depends on the investigated reaction product. $z = 2$ for the methanol oxidation to formaldehyde and $z = 4$ for formic acid.

$$n_{\text{theo}} = \frac{Q}{zF} \quad (4.3)$$

The charge Q was calculated with the applied current and the reaction time according to Equation 4.4.

$$Q = I \cdot t \quad (4.4)$$

If the experiment was repeated multiple times, the average was calculated and the standard deviation is shown in error bars in the graphs. If no error bars are shown, the experiment was only conducted once.

Calculation of the specific energy consumption: The specific energy consumption correlates the energy input to the amount of product formed (Equation 2.3, see also section 2.1). The Faraday efficiency was calculated as described in the previous paragraph. The potential of the experiment was averaged over its duration via the Gamry Echem Analyst (version 7.10.0). If the experiment was repeated multiple times, the standard deviation were obtained for the Faraday efficiency (ϕ) and the cell potential E_{cell} . The uncertainty for E_s was calculated via the propagation of uncertainty (Equation 4.5). The stoichiometric factor for the oxidation of methanol to formaldehyde is $\nu_p = 1$.

$$\begin{aligned} \Delta E_s &= \frac{\delta E_s}{\delta E_{\text{cell}}} \Delta E_{\text{cell}} + \frac{\delta E_s}{\delta \phi} \Delta \phi \\ &= \frac{zF}{\phi \nu_p} \Delta E_{\text{cell}} + \left(-\frac{E_{\text{cell}} z F}{\phi^2 \nu_p} \Delta \phi \right) \end{aligned} \quad (4.5)$$

4.3 Analytical methods

Several analytical methods were used in this work to investigate the reaction products, the physical properties of the electrolyte solution, the water content in the electrolyte, the electrode surface and adsorbed species during the electrochemical reaction. The used methods, machines and operation conditions are described in detail in the following sections.

4.3.1 High-performance liquid chromatography

High-performance liquid chromatography (HPLC) is a versatile and commonly used analytics method to separate the compounds of a sample mixture. After the HPLC separation, the individual substances are detected and the quantities can be determined if a suitable calibration is available. HPLC is a physical separation method. A chromatography consists of a stationary phase, which can be a solid, a liquid or a gel and a mobile phase. The separation properties of the stationary phase can be adjusted by changing its grain size and surface functionalization. The mobile phase consists of the eluent and the sample. The eluent is a constantly fed solvent that moves along the stationary phase in a defined direction. The separation performance of the HPLC depends on the interactions between the stationary phase and the sample molecules. The separation is achieved due to molecule specific properties such as adsorption, dissolution or a selective reversible reaction. A schematic illustration for an HPLC column that works via a selective reversible reaction is shown in Figure 4.7.^[164]

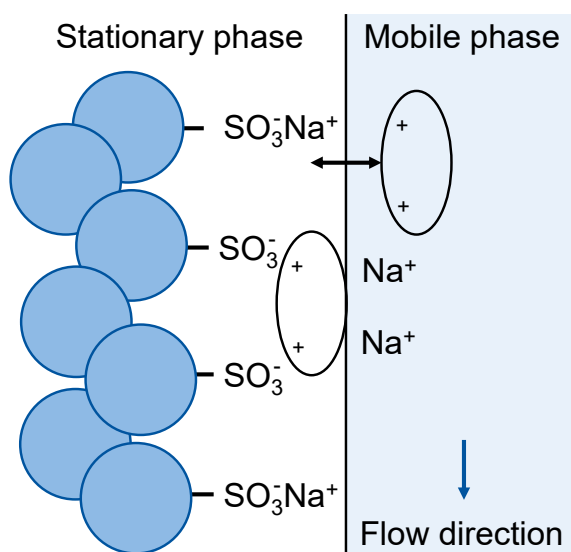


Figure 4.7: Schematic illustration of ion exchange chromatography. Adapted from Naumer *et al.*^[164]

The separation of the displayed HPLC system functions via ion exchange and adsorption of the particles in the mobile phase. The stationary phase contains ionic functional groups that can interact with the mobile phase via reversible exchange reactions. The sample compounds can replace the mobile cations that coordinate to the immobilized anions on the stationary phase. This interaction strength depends on the molecular radius and charge of the coordinating substance. Opposite charges between the substance and the stationary phase lead to a strong attractive interaction. Strong

interactions mean that the substance moves along the stationary phase more slowly, so it has a longer retention time. The molecular radius is a parameter for the molecules polarizability with larger molecules being more easily polarized. A highly polarizable molecule can strongly interact with the stationary phase as partial charges can be distributed more easily. The ion size is often different even if the molecules are otherwise chemically similar. Besides the ionic interactions, physical adsorption also occurs due to weak Van-der-Waals forces between the stationary and mobile phase.^[164]

The HPLC samples in this work were analyzed via an HPLC Agilent 1260 with an organic acid column (250 mm length, 8 mm diameter, CS Chromatographie Service GmbH). The column is filled with a modified styrene-divinylbenzene-copolymer with a particle size of 10 μm . The column was stored in 5 mmol H_2SO_4 in ultra pure water, which was also the eluent. During operation, the column was heated to 40 $^\circ\text{C}$ and the eluent is fed with a flow rate of 0.5 mL min^{-1} . The pressure on the column is approximately 70 bar. Before measuring the sample, formaldehyde and formic acid standards were run on the column to determine the accurate retention times as they can shift due to column aging. In a new column, the retention times are longer. After some usage, the retention time of formaldehyde is 16.4 min and 17.5 min for formic acid. Methanol had a retention time of 23.3 min. The injection volume of the sample was 2-10 μL depending on the expected formaldehyde concentration to stay within in the calibration limits. This had the additional benefit to reduce the methanol load on the column as too high methanol concentrations damage the packing material. The measuring time for one sample is 35 min. The products were analyzed with a refractive index detector (RID) after the column. The HPLC was calibrated for formaldehyde and formic acid so the peak size can be correlated to a concentration. For the calibration, a dilution series was prepared for each substrate. These samples with known concentrations were measured and the recorded refractive index signal depends on the substrate concentration. Based on these measurements, the RID signal can be correlated to the concentration of formaldehyde (1-1000 g L^{-1}) or formic acid (2-999 g L^{-1}), respectively (Figure 4.8). The formaldehyde peak can overlap the formic acid peak due to tailing. This can lead to an overestimation of both concentrations, especially when they are only present at low concentrations. Whenever formaldehyde is produced in much larger quantities (≥ 5 times), formic acid only appears as a peak shoulder, which makes it not quantifiable (Figure 4.8 b)). To avoid overestimation of the formed products, the peaks were only integrated over the retention time of the pre-sample standard. Any area that tailed beyond the peaks of the standards was not taken into account in the analysis. Each HPLC sample was measured twice to account for measurement inaccuracies.

Double analysis of nine different samples containing $5\text{--}7\text{ g L}^{-1}$ formaldehyde showed a measuring error of $\pm 0.04\text{ g L}^{-1}$ or 1 %.

Other possible side products such as oxymethylene ether (chain length = 2), trioxane or methoxymethanol were not detected in the HPLC. The HPLC samples were analyzed by Timo Linzenmeier, Frederike Schiszler and Justin Gottfried (Central Analytical Laboratory, Aachener Verfahrenstechnik, RWTH Aachen University).

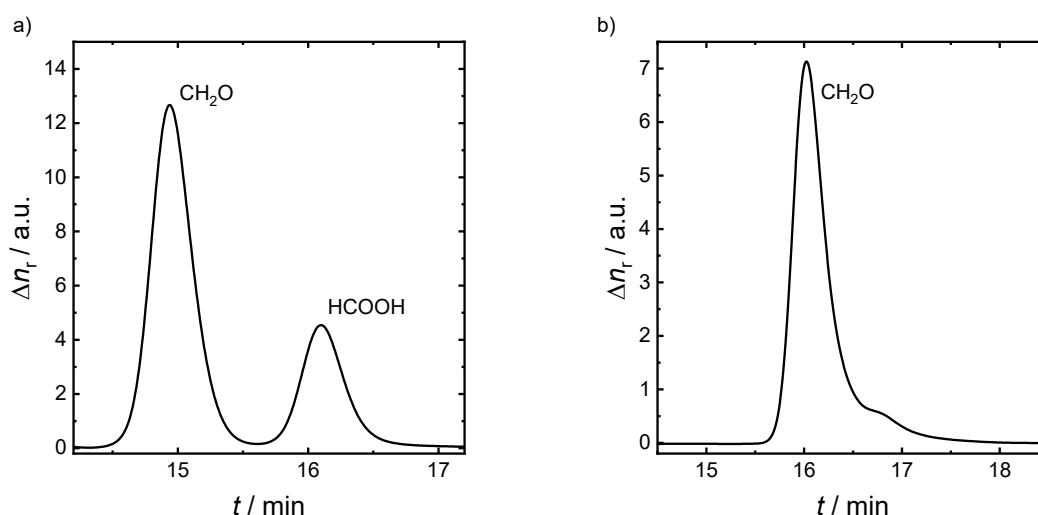


Figure 4.8: Exemplary measuring curves for two samples containing a) formaldehyde and formic acid and b) mainly formaldehyde, so formic acid appears as a peak shoulder.

4.3.2 Gas chromatography

To analyze gaseous side products that formed during the reaction, samples were analyzed via gas chromatography (GC). GC functions based on the same concepts as HPLC. However, the sample is now provided in a gaseous state. The stationary phase can be either solid or liquid. Similar to HPLC, the separation can occur due to adsorption, dissolution and selective reversible reactions but also due to separation by different boiling points.

CO and CO₂ are possible products of the MOR. To investigate whether they formed during the reaction, a gas-collection bag was connected to the electrolyte reservoir. The tube inlets to the electrolyte reservoir were wrapped in parafilm to improve tightness. The experiment was conducted in 0.1 mol L^{-1} and 1.0 mol L^{-1} NaOMe at 100 mA cm^{-2} for 45 min. The collected gas was analyzed for H₂, CO and CO₂. The GC measurements in this work were taken with a GC Agilent 8860. Three different columns (Haysep Q,

CP-Sil 5CB, MS5A) are used. The Haysep Q and molsive MS5A columns separate H_2 , CO and CO_2 , which are detected via a thermal conductivity detector. The CP-Sil 5CB column is able to separate methane and ethylene and used a flame ionization detector. The initial column temperature is $50^\circ C$ that was hold for 7 minutes and afterwards the temperature increased to $150^\circ C$ with a heating rate of $15^\circ C\ min^{-1}$. The eluent was helium. The samples were analyzed by Sandra Gelbach (Department of Chemical Process Engineering, RWTH Aachen University).

4.3.3 Scanning electron microscopy

Scanning electron microscopy (SEM) can be used to analyze the surface structure in the mm to nm range. In SEM, electrons are accelerated in an electric field and the beam is shot at the sample. This leads to backscattering of beam electrons, removal of sample core electrons (secondary electrons) and X-ray emissions. The secondary electrons are most important to investigate the surface structure as they contain information about the sample morphology and topography. The backscattered electrons can be used to highlight contrasts in multi-element samples as heavier elements cause more backscattering. The X-ray emissions are element specific and can be used to determine the sample composition on the surface.^[165]

The surface topography was investigated using a Hitachi Table Top TM 3030 Plus scanning electron microscope (SEM) with an energy dispersive X-ray detector (EDX, Bruker Quantax 70). The electron acceleration voltage was 15.0 kV. Images were taken at magnifications of 1000, 2000 and 4000. Measurements were performed by Karin Faensen (Central Analytical Laboratory, Aachener Verfahrenstechnik, RWTH Aachen University).

4.3.4 Conductometer

The ionic conductivity of the electrolyte is an important parameter in electrochemical cells. It is reciprocal to the resistance and it describes how easily a charge is transported through the electrolyte. A high conductivity means that lower potentials can be achieved, which lowers the energy requirement of the electrochemical reaction. The conductivity of the electrolyte strongly depends on the number of dissociated ions as they transport the charge and how easily they can move through the electrolyte. The

degree of dissociation majorly depends on the permittivity of the solvent. The ion mobility depends on several factors such as ion size, charge, concentration, solvent viscosity and temperature.

To measure the conductivity of the electrolyte, an AC potential is applied in a two electrode setup and the current response is measured. The AC is applied to minimize the formation of an ion-double layer on the electrodes, which adds artificial resistance. The conductivity κ of the electrolyte can be determined by measuring the resistance R with respect to the length of measurement path (d) and the area (A). The correlation between these quantities is shown in Equation 4.6.^[166] R is calculated from the applied potential and the current response according to Ohm's law (Equation 2.4).

$$\kappa = \frac{1}{R} \cdot \frac{d}{A} \quad (4.6)$$

The Metrohm 712 conductometer was calibrated with 11.67 mS cm⁻¹ KCl solution. The conductivities of 0.1 mol L⁻¹ and 1.0 mol L⁻¹ NaOMe, LiOMe, NaClO₄ and LiClO₄ were measured at 21 °C. Two different samples of NaOMe and NaClO₄ were measured and the average values are displayed with the standard deviations as error bars. The error of determination of the conductometer is $\pm 40 \mu\text{S cm}^{-1}$, which was estimated based on triple measurements of the 0.1 mol L⁻¹ NaOMe solution.

4.3.5 Rheometer

A rheometer was used to determine the viscosity of liquid samples. Different viscosities originate from intermolecular interactions. To determine the viscosity of a liquid, two plates are in close proximity of each other and the gap between is filled with the liquid sample. One of these plates rotates which shears the liquid. The response of the liquid is defined by its viscosity with more viscous liquids requiring a higher torque to maintain the rotation speed. The torque is measured continuously and can be used to calculate the viscosity.^[167]

The Anton Paar MCR 102 rheometer was equipped with a Double Gap DG42/Q1 measuring system that allows the analysis of low viscous liquids. The experiments were carried out with 20 mL sample volume and the temperature was kept constant at 20 °C during the measurement. The viscosity of pure methanol and NaOMe, LiOMe, NaClO₄ and LiClO₄ were measured at two concentrations (0.1 mol L⁻¹ and 1.0 mol L⁻¹). Each sample was measured three times to determine the error of determination ($\leq 4 \mu\text{Pa s}$).

4.3.6 Attenuated total reflection surface-enhanced infrared absorption spectroscopy

Attenuated total reflection (ATR) surface-enhanced infrared absorption spectroscopy (SEIRAS) is a powerful spectroscopy method that allows a time resolved analysis of surface species.^[168,169] Infrared (IR) spectroscopy is based on the molecular adsorption of electromagnetic radiation in the IR range. The adsorbed energy increases the energy level of molecule-specific vibrational modes that can be detected.^[169] ATR is a variant of IR spectroscopy to analyze the interface of a dielectric medium with a high refractive index (ATR element) and the sample. If the IR beam meets the sample at a certain angle, it is reflected on the sample surface and forms an evanescent wave (Figure 4.9).^[170]

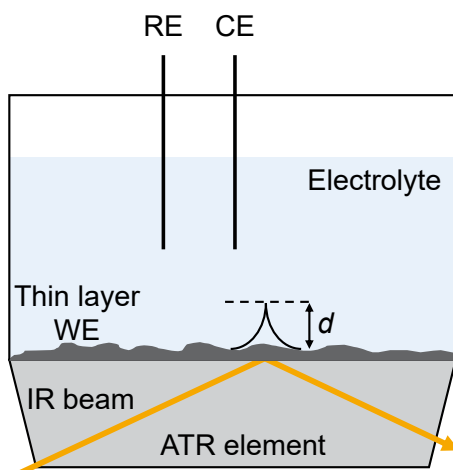


Figure 4.9: Schematic diagram of an ATR-SEIRAS cell. Adapted from Kas *et al.*^[169]

This evanescent wave penetrates a few micrometers into the sample that is on top of the dielectric ATR element. As the evanescent wave reaches a few micrometer into the IR adsorbing sample, it can be used to analyze surface species on an electrode in the range of the electrochemical double layer. The penetration depths can be adjusted by the wavelength, the angle of incidence and the refractive indices of the ATR element and the electrolyte.^[169] To realize the electrochemical *in-situ* ATR-SEIRAS measurements, ATR elements are covered with thin metal films that function as the electrode.^[169,171] The use of sufficiently thin metal films limits the penetration depths of the evanescent wave to one adsorbed monolayer on the surface while also enhancing the recorded IR signal.^[169,172–174] It is important to note that the electric field during the electrochemical measurement can shift the baseline and peaks of the ATR-SEIRAS

measurement.^[175,176] This needs to be taken into account when analyzing the obtained IR spectrum.

The ATR-SEIRA spectra in this work were recorded using a Vertex70 spectrometer with a mid-IR source, a KBr beamsplitter and a nitrogen-cooled mercury cadmium telluride detector. Prior to the electrochemical experiment, the whole spectrometer and measurement optics were purged with nitrogen for 10 min. The beamline was also continuously purged during the experiment. The electrochemical cell was attached to a jackfish VeeMAX III optical cell from pike technologies (Figure 4.10).



Figure 4.10: Picture of the H-cell in the ATR setup.

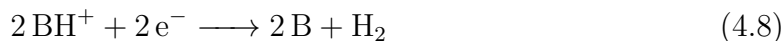
A silicon wafer was used as the ATR element that was coated with Pt, which was also the WE. The wafer was secured in the cell using an O-ring seal. Two Au pins led outside of the cell for electrical contact. The electrochemical cell was attached to the Pt WE with another O-ring seal. To complete the cell setup, a Pt wire was used as the CE and a Ag wire was used as a pseudo-RE. The cell was filled with 45 mL of

pure methanol to measure the background. Afterwards, the IR spectra in 0.1 mol L⁻¹ NaOMe, 1.0 mol L⁻¹ NaOMe and 0.1 mol L⁻¹ NaClO₄ were measured. A Gamry 3000 potentiostat was used to apply potentials of 0.7 V, 1.3 V and 2.4 V vs fc. The potential variation was only measured in 1.0 mol L⁻¹ NaOMe, all other measurements had an applied potential of 2.4 V vs fc. Each spectrum was recorded for 30 s with a resolution of 4 cm⁻¹, which consists of approximately 64 scans that were averaged with the Bruker Opus software (version 4.0). Ten subsequent spectra were recorded, the first and the last two were recorded without an applied potential. The CA measurement was performed for 180 s starting with the third spectrum. The measurements were performed in collaboration with Nils Kurig (Institute of Technical and Macromolecular Chemistry, RWTH Aachen University).

4.3.7 Karl Fischer coulometry

This work investigated the MOR in anhydrous methanol. Because of the hygroscopic properties of methanol, the water content of the most commonly used electrolytes was determined with a Karl Fischer coulometer 831 by Metrohm using Hydranal Coulomat E as reagent.

For the Karl Fischer reaction, I₂ is stoichiometrically used up for each H₂O in the sample. In the Karl Fischer coulometry, the reagent solution contains iodide I⁻, a short-chain alcohol (e.g., methanol or ethanol), a base (B, e.g., pyridin or imidazole), and SO₂. The Karl Fischer reaction requires I₂ that is generated galvanostatically at the anode (Equation 4.7) with hydrogen evolution from the protonated base occurring on the cathode (Equation 4.8).^[177]



In the alkaline Karl Fischer reagent, SO₂ reacts with the alcohol to a sulfite-ester. The example reaction is given for methanol.^[177]



The sulfite ester is oxidized by iodine and water in the presence of a base to the sulfate-ester and the iodide-protonated-base salt. Thus, the iodide-cation pair that is used up in the electrochemical reaction is reformed.^[177]



The detection is carried out by a second set of two Pt wire electrodes. On these electrodes, the oxidation of iodide to iodine (Equation 4.7) and the reduction of iodine to iodide occur (Equation 4.11).



In the beginning, only little current flows between these electrodes as the iodine reacts in the Karl Fischer reaction and no other cathode reaction is available at the potential. Once no more water is present in the solution, the I_2 concentration increases and current starts flowing between the two detection electrodes and the coulometry is complete.^[177]

The Karl Fischer coulometer was calibrated with a water standard of 0.1 wt.% and seven repeated measurements averaged 0.102 wt.% water with a standard deviation of 0.0054 wt.%.^[178]

The water content of freshly prepared samples of pure methanol, 0.1 mol L⁻¹ and 1.0 mol L⁻¹ NaOMe was determined. The samples were measured three times each (Table 4.1) and the experimental deviations are within the setup deviations. Only NaOMe electrolytes were measured because they were prepared by diluting a 5.4 mol L⁻¹ NaOMe in methanol solution. All solid electrolytes were dissolved in methanol, so the water content of the pure methanol was assumed.

Table 4.1: Measured water contents of different electrolytes.

Solution	wt.% H ₂ O
MeOH	0.0092 ± 0.0008
NaOMe 0.1 mol L ⁻¹	0.0180 ± 0.0004
NaOMe 1.0 mol L ⁻¹	0.0435 ± 0.0008

5 Investigation of water-free reference electrodes

REs are a fundamental tool that is used to measure individual electrode potentials in an electrochemical cell. Thus, a suitable RE is required that provides a reliable and stable potential. The RE potential can be influenced by liquid junction potentials (LJPs), which can occur if different ions or solvents are present in the RE and the measuring cell. In non-aqueous media, Ag/Ag^+ REs are often applied and their reference potentials are given vs the half-wave potential of the ferrocene/ferrocenium (fc/fc^+) redox couple, which is noted as E vs fc (see also subsection 2.2.2). Thus, the LJP influence of different ions in the RE compartment was investigated in methanol-based Ag/Ag^+ REs. Though Ag/Ag^+ REs are often used in literature, they are only stable for a short time (1-2 weeks).^[52,71] In aqueous electrolytes, Ag/AgCl REs are commonly used electrodes that are long term stable. They promise a potentially more stable reference potential than the Ag/Ag^+ REs. To improve the stability, two different methanol-based Ag/AgCl REs were built and their stability and impedance were compared with an Ag/Ag^+ -RE and a Ag wire pseudo RE.

5.1 Influence of different ions in Ag/Ag^+ reference electrodes

Ag/Ag^+ REs are common electrodes for use in anhydrous reaction environments. They can be filled with the same solvent as the electrochemical cell avoiding potentially high LJPs.^[52,74,88] Still, LJPs can also occur in identical solvents if there is a concentration gradient present due to differing ion mobility.^[52] To gain a better understanding on how individual ions influence the LJPs in Ag/Ag^+ REs, several Ag/Ag^+ REs were manufactured containing different Ag salts and supporting electrolytes. The RE contained

one of either Ag salt (AgNO_3 or AgClO_4) and one supporting RE electrolytes (el_{RE} , NaClO_4 , LiClO_4 , TBAP). The half-wave potential ($E_{1/2}$) of fc/fc^+ was determined in an H-cell that contained one of two different supporting cell electrolytes (el_{cell} , LiClO_4 or NaClO_4) in addition to fc . An overview of the possible combinations is shown in Figure 5.1.

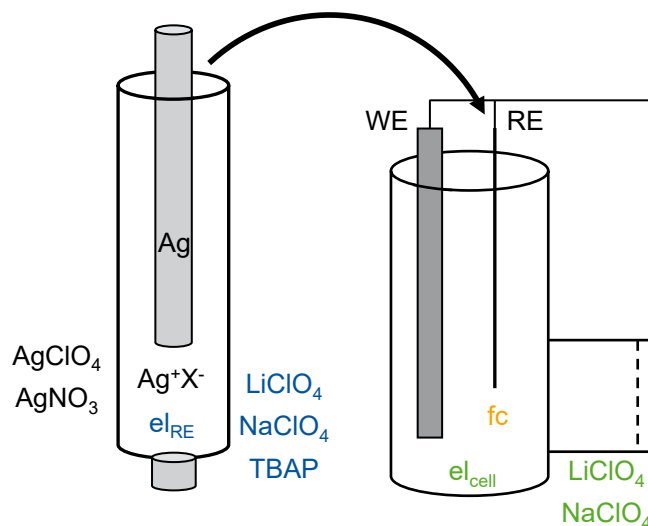


Figure 5.1: Schematic overview about silver salts and the supporting electrolytes in the Ag/Ag^+ REs (el_{RE}) and the electrolyte cell (el_{cell}).

CVs were measured for all combinations of Ag salts, el_{RE} and el_{cell} and the half-wave potential $E_{1/2}$ of fc/fc^+ was calculated according to Equation 2.9. $E_{1/2}$ for all Ag/Ag^+ REs is shown in Figure 5.2. Figure 5.2 a) shows the results measured in LiClO_4 as el_{cell} . All REs provided a stable and reproducibel half-wave potential within ± 5 mV. The average $E_{1/2}$ for the different electrodes can be summarized as -177 ± 5 mV except AgNO_3 with LiClO_4 as el_{RE} , which has a $E_{1/2}$ of -167 mV. The similar potentials indicate comparable LJPs for the different Ag salts and supporting RE electrolytes when the cell contains LiClO_4 . It is also possible that the LJPs only provide a small contribution to the overall RE impedance.

Using NaClO_4 as the supporting cell electrolyte (Figure 5.2 b)), larger differences for the half-wave potentials are observed for both, the Ag salts and the supporting RE electrolytes. Only TBAP as the supporting RE electrolyte leads to similar half-wave potentials for both Ag salts. In contrast, the RE containing AgClO_4 with el_{RE} NaClO_4 in measured in el_{cell} NaClO_4 has a standard variation of the $E_{1/2}$ of ± 7 mV. This variation of $E_{1/2}$ is too large to be considered reliable.^[70] In comparison, the variation of the half-wave potential across all REs is smaller when LiClO_4 is used as the cell electrolyte. A reason for these differing potentials with the NaClO_4 cell electrolyte can

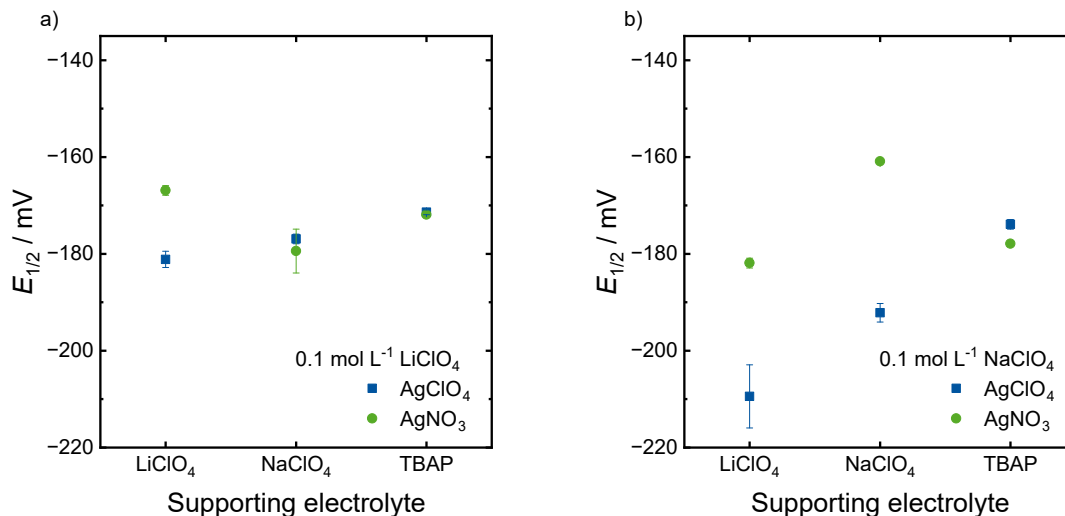


Figure 5.2: Half-wave potentials of fc in transparent electrode compartments for combinations of AgClO₄, AgNO₃ and el_{RE} (LiClO₄, NaClO₄, TBAP) in the el_{cell} a) 0.1 mol L⁻¹ LiClO₄ and b) 0.1 mol L⁻¹ NaClO₄ in methanol. Each RE was prepared twice and the averages are shown with the standard deviation.

be a higher LJP sensitivity or increased frit clogging. Note that the measurements with the NaClO₄ cell electrolyte were conducted after the experiments in LiClO₄, which could also lead to an increased aging or frit clogging by precipitation. The Ag precipitation can cause higher LJPs by frit clogging and also lower the amount of Ag ions in the RE compartment, which alters the chemical activity of the remaining Ag⁺ ions. To inhibit the precipitation caused by UV-light and improve the stability of Ag/Ag⁺ REs, the study was repeated with brown glass RE compartments. The half-wave potentials of the brown glass REs are shown in Figure 5.3. Overall, less variation between different Ag salts and supporting electrolytes (el_{RE} and el_{cell}) can be observed compared to the transparent RE vials (Figure 5.3). As all potentials were between -170 mV and -150 mV, it appears that the LJPs are less influential using the brown glass RE compartments. Also, no significant spread of the RE potentials in 0.1 mol L⁻¹ NaClO₄ as el_{cell} (Figure 5.3 b)) is observed. Thus, it is likely that clogging did not occur. However, the brown glass REs showed a stronger leakage than the commercial Ag/Ag⁺ REs, which might have caused the larger error bars compared to the transparent compartments. For a reliable RE, a potential window of ± 5 mV is considered stable. Yet, the error of the brown glass REs is often close to or above this stability threshold.

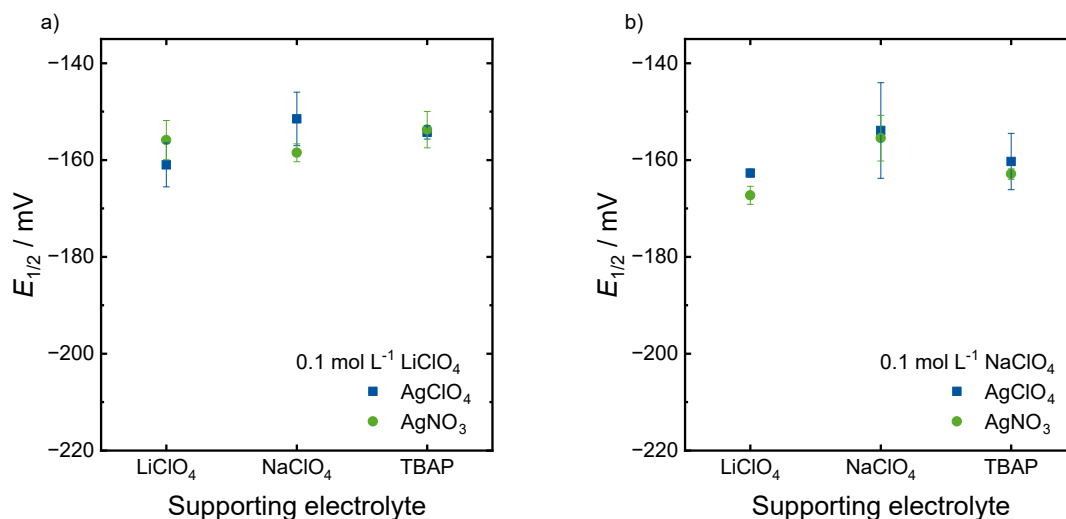


Figure 5.3: Half-wave potentials of fc in dark electrode compartments for combinations of AgClO₄, AgNO₃ and el_{RE} (LiClO₄, NaClO₄, TBAP) in the el_{cell} a) 0.1 mol L⁻¹ LiClO₄ and b) 0.1 mol L⁻¹ NaClO₄ in methanol. Each RE was prepared twice and the averages are shown with the standard deviation.

Though it was possible to reduce the ion influence on the electrode potential by using the brown glass RE compartments, the leakage can cause cross-contamination of ions to the measuring cell. Thus, the transparent RE vials were used for further experiments. To minimize potential ion contamination, the use of AgClO₄ with either LiClO₄ or NaClO₄ as supporting RE electrolytes is recommended for a perchlorate-base cell electrolyte. Using the brown glass RE compartments was not successful to increase the stability of Ag/Ag⁺ REs, so other alternatives have to be investigated.

5.2 Characterization and comparison of methanol based reference electrodes

In the previous chapter, the ion influence on the LJPs of Ag/Ag⁺ REs was investigated. However, these type of REs are only short term stable.^[52,71] Thus, alternative Ag-based REs are explored for use in anhydrous methanol. To find a stable and easy to use RE with a low impedance, four different home-made REs were tested for their applicability in AC and DC measurements. The potential and stability of these REs was determined by measuring the half-wave potential of the fc/fc⁺ redox couple over a time of 49 days.

The RE's impedance was determined with EIS over a span of 7 days and its influence on DC and AC measurements was analyzed.

Four different types of REs were prepared. The 1st type is a Ag/AgCl RE with the addition of small amounts of water as described by Brossia *et al.*^[161] The 2nd type was prepared analog to an Ag/AgCl RE for use in an aqueous environment, but stored in methanol. The 3rd type is a Ag/Ag⁺ RE with minimized LJPs based on previous results was used as it is the literature standard for use in anhydrous electrochemistry.^[91–93] The 4th type is a Ag wire as a pseudo-reference electrode. To guarantee the reproducibility of the REs, two electrodes of each type were prepared except for the Ag wire. A detailed overview of the REs and the storage conditions can be found in Table 5.1.

Table 5.1: Overview about the different REs and the storing conditions. All REs were stored in methanolic electrolytes, except the Ag wire, which was cleaned with sandpaper.

Type	RE	Electrode	Stored in
1 st	1 & 2	Ag/AgCl	0.1 mol L ⁻¹ LiCl 0.66 mol L ⁻¹ H ₂ O
2 nd	3 & 4	Ag/AgCl	0.1 mol L ⁻¹ LiCl
3 rd	5 & 6	Ag/Ag ⁺	0.1 mol L ⁻¹ LiClO ₄ 0.01 mol L ⁻¹ AgClO ₄
4 th	7	Ag wire	dry

5.2.1 Stability measurements

To determine the fc/fc⁺ half-wave potential of the REs, CVs were measured immediately after assembly at scan rates of 50, 100, and 200 mV s⁻¹. The fc/fc⁺ redox curves for each type of RE are shown in Figure 5.4. The CV curves of Ag/AgCl with and without water were overlapping, and thus, the CV curves of the non-aqueous Ag/AgCl are omitted for clarity. The $E_{1/2}$ for the fc/fc⁺ redox couple are scan-rate independent proving the reaction's reversible character for all tested REs.^[69] The fc/fc⁺ redox potentials, however, differ for each type of RE. The Ag/Ag⁺ RE provides the only negative fc/fc⁺ redox potential, whereas the Ag wire with the same electrode reaction shifted to higher potentials by 350 mV to $E_{1/2} = 185$ mV. This potential shift is caused by the different reaction environments as Ag⁺ cations are present in a much higher concentration with the solvated AgClO₄ for the Ag/Ag⁺ RE. The Ag/AgCl REs show the highest fc/fc⁺ redox potential (~400 mV) ?caused by the different reference electrode reaction of $\text{AgCl} + \text{e}^- \rightleftharpoons \text{Ag} + \text{Cl}^-$.

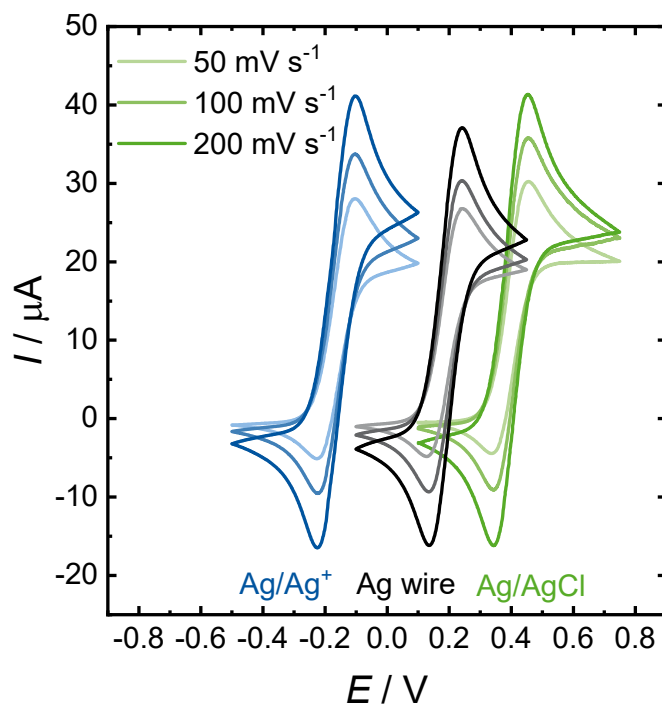


Figure 5.4: CVs of different Ag-based REs (Ag/Ag^+ (blue), Ag wire (black), Ag/AgCl (green),) in $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$ and $5 \text{ mmol L}^{-1} \text{ fc}$ in methanol at different scan rates. The 5th cycle is shown of each CV-series.

The fc/fc^+ redox potentials were determined for 5 consecutive days after construction and then repeated weekly until day 49 except RE 7. Each data point corresponds to the mean values of $E_{1/2}$ averaged for the 5th cycle across all scan rates and the error bars show the standard deviation (Figure 5.5). The average of the first 14 days was taken and is indicated in a gray line with the dotted lines indicating a $\pm 5 \text{ mV}$ stability window.

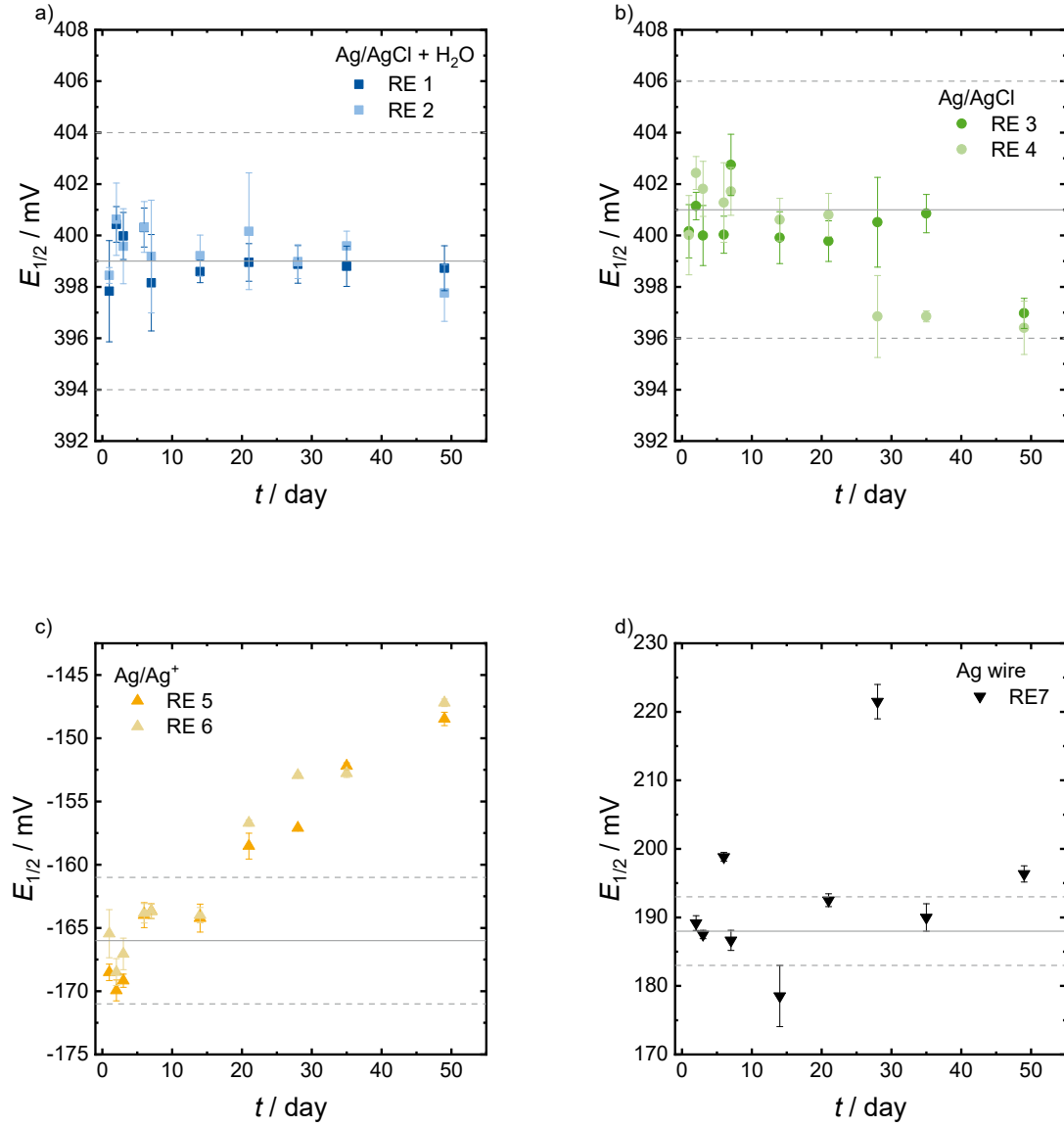


Figure 5.5: $E_{1/2}$ of a) Ag/AgCl REs with H₂O, b) Ag/AgCl REs without H₂O, c) Ag/Ag⁺ REs and d) Ag wire. The solid line indicates the average over the first 14 days. The dotted lines indicate a stability interval of ± 5 mV.

For the type 1 REs (Figure 5.5 a)), the average potential of the first 14 days is 399 mV. RE 1 & 2 remained stable throughout the 49 days with a high agreement among all measured potentials.

RE 3 & 4 show an average $E_{1/2}$ of 401 mV over the first 14 days (Figure 5.5 b)). A slight deviation compared to RE 1 & 2 was expected because of different H_2O contents and the interrelated different solvation energies and activities of chloride ions in methanol and water.^[52,161] However, the average potential difference is only 2 mV s^{-1} . All mean values of the type 2 REs are inside of the stability window of $401\pm 5\text{ mV}$ except for the error bars of two RE 4 measurements exceeding the stability window. This was likely caused by a leakage of the supporting electrolyte solution leading to a significantly lower solvent volume for RE 4 after 28 days. The $E_{1/2}$ of RE 3 also dropped after 49 days even though it remained within the stability window. It has to be verified whether type 2 electrodes are stable for this extended amount of time. Taking the leakage into account, the stability of the non-aqueous REs 3 & 4 is comparable to RE 1 & 2 for the first three weeks.

The average $E_{1/2}$ of RE 5 & 6 of the first 14 days was $-166\text{ mV}\pm 2\text{ mV}$ (Figure 5.5 2c)). The measured potentials range from -170 mV to -164 mV within the first 7 days. However, there is a constant shift towards higher potentials of 0.4 mV day^{-1} until the half-wave potential reaches -148 mV after 49 days. A gray discoloration was observed at the frit of both REs, which gradually darkened over time. The discoloration is likely caused by the precipitation of elemental Ag. It is reported that Ag/Ag⁺ electrodes need to be prepared freshly to guarantee reliable measurements as the potential shifts can reach a few ten millivolts after several days.^[71] Thus, the Ag/Ag⁺ electrodes allow accurate measurements for 14 days but require more maintenance compared to the Ag/AgCl REs.

The pseudo-reference electrode (RE 7) shows the highest fluctuation for the half-wave potential across the 49 days (Figure 5.5 2 d)). Although five of the nine measured potentials are within the stability window of $188\pm 5\text{ mV}$, the high fluctuation require daily inspection of the Ag wire's half-wave potential and the stability within one measurement cannot be guaranteed.

The experiments show the best stability for the Ag/AgCl-based REs, which were stable for at least 49 days. The completely non-aqueous REs 3 & 4 showed a similar behavior, but it needs to be verified for how long they are stable. Thus, the completely water-free REs are a valid alternative to avoid any kind of aqueous cross-contamination with the reaction solution, but as all REs they need to be checked regularly.

5.2.2 Impedance measurements

The impedance of all 7 REs was investigated with electrochemical impedance spectroscopy (EIS) in a frequency range of 5 kHz to 100 Hz by using the RE as WE.^[80] Measurements were carried out on day 1-3, 6 and 7 after construction. The data point with the lowest reactance (imaginary part) was chosen to compare the different electrodes as it best describes contributions of the the real resistance to the total RE impedance (Equation 2.8, example shown in a Nyquist plot in Figure 5.6).

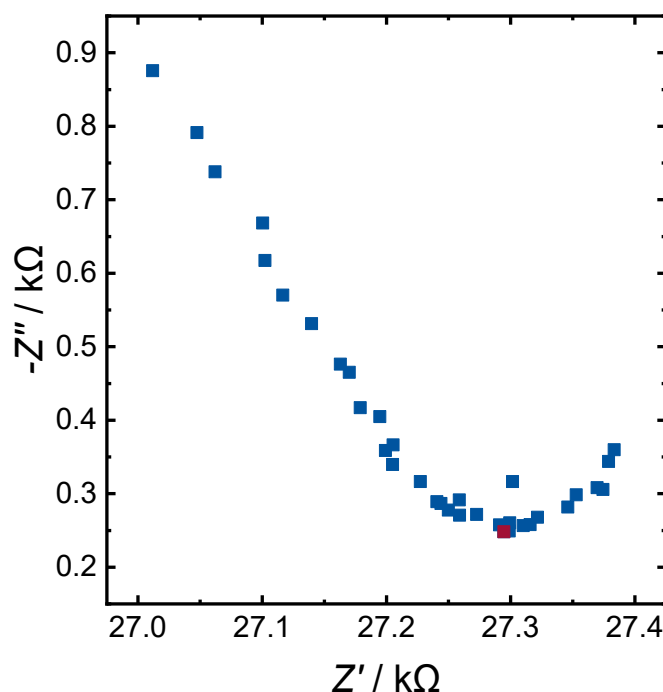


Figure 5.6: Nyquist plot of RE 1 on day 7. The data point with the lowest imaginary impedance is marked in red.

All REs have negative reactances, which indicates capacitive effects. These capacitive effects likely caused by the electrochemical double layer formation as well as the frit junctions. The negative sign is a result of the phase shift's direction, yet, the reactance always increases the overall impedance, and thus, all impedances are given as positive values (see also subsection 2.2.2). The impedance of the REs varies vastly between the different RE types (Figure 5.7). All the impedances, resistances, reactances and phase angles are shown in Table A.4-Table A.10.

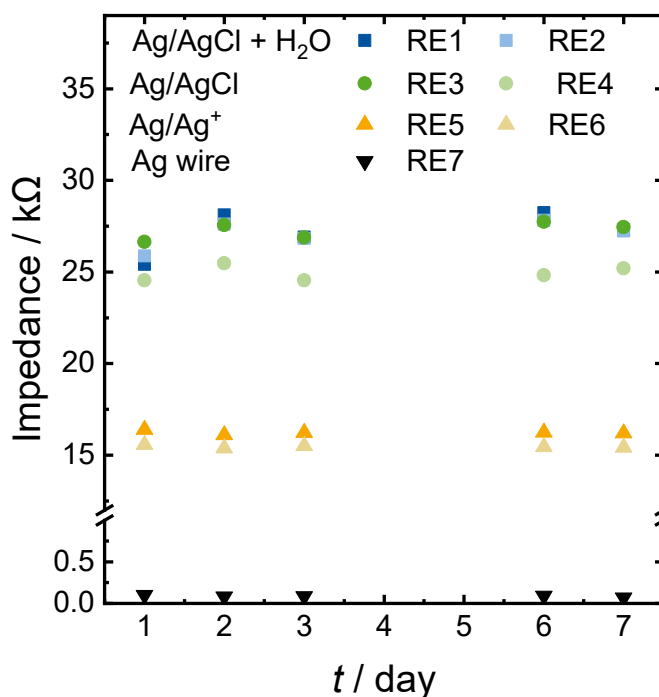


Figure 5.7: Impedance of the different REs over the course of 7 days after their construction.

The impedance for the Ag/AgCl electrodes is the highest and ranges between 25-28 kΩ. Only an insignificant difference between the aqueous containing RE 1 & 2 and the non-aqueous RE 3 can be observed. RE 4 has lower impedances, which are likely caused by a damaged frit. The phase angles are between -0.6° and -0.3° with reactances between $150\ \Omega$ and $300\ \Omega$. The Ag/Ag⁺ electrodes (RE 5 & 6) show significantly lower impedances between 15-16 kΩ, which were constant over 7 days. The lower resistances might be caused by a higher conductivity of the electrolyte solution. The phase angles were between -0.8° and -0.6° . The reactances ranged between $150\ \Omega$ and $200\ \Omega$. The Ag wire has the lowest impedance between $80\text{--}100\ \Omega$ as it has no filling solution, no frit or LJP and is, thus, more responsive to high frequency AC. It has, however, the largest phase angles between -5° to -10° . This is also reflected in the comparably large reactances of about $10\ \Omega$, which are proportionally larger compared the RE 1-6. The small phase angles of the RE types 1-3 indicate that the reactance provides only a minor contribution to the total RE impedance. This is also shown in the Bode plots (Figure A.1) that show an independent RE impedance with regard to the AC frequency. For the Ag wire impedance, the capacitive influences cannot be neglected, which is reflected in the frequency dependent impedance of RE 7. As the resistance of

a capacitor decreases with increasing AC frequencies, the lowest impedance for the Ag wire was measured at the highest frequency.

To evaluate these impedances in a real system, their effects on DC and AC applications were calculated. These calculations only consider the RE impedance and the potentiostat detection limitations, so they are the minimal expected setup error for the respective DC and AC measurements. The impedances used in the calculations are the respective RE impedances averaged over the 5 measurements.

DC measurements are affected by the leakage current flowing through the electrometer input, which measures the potential difference between the electrodes. In modern potentiostats, the electrometer input current is estimated at 50 pA.^[70] The DC measurement error on the potential can then be calculated according to Ohm's law (Equation 2.4) with the electrometer input current and the RE impedance (Table 5.2). The potential error of RE 1-6 is about 1 μ V and, for the Ag wire, it is in the nV-range. AC measurements are affected by the RC low pass filter between the RE and the potentiostat reference input. Above a certain frequency, the potential falls off over the resistance and instead of the capacitor and the measured potential becomes damped (see also subsection 2.2.2). This frequency threshold is called cutoff frequency f_c and it can be calculated according to Equation 5.1. The capacitance C of the reference input is set as 5 pF^[80] and the calculated f_c are also shown in Table 5.2.

$$f_c = \frac{1}{2\pi ZC} \quad (5.1)$$

Table 5.2: Influence of the RE impedances on potential accuracy and the cutoff frequency.

RE	Z_{av} Ω	U_{error} μ V	f_c MHz
1	27196	1.36	1.17
2	27077	1.35	1.18
3	27249	1.36	1.17
4	24911	1.25	1.28
5	16226	0.81	1.96
6	15462	0.77	2.06
7	86	0.01	369.81

The f_c for the Ag/AgCl-based electrodes is around 1.2 MHz and, thus, only applicable for AC currents with lower frequencies. The Ag/Ag⁺ REs have a higher f_c of 2 MHz due to their lower impedances. The highest f_c was determined for the Ag wire with

369 MHz. Please note that all these calculations provide the maximal f_c introduced by the potentiostat and the RE. Real f_c are likely smaller as they contain other setup effects, such as resistances and capacitances caused by cables and signal amplifiers in the potentiostat and double layers on the electrodes.

5.2.3 Summary of the reference electrode comparison

In this chapter, two types kinds of methanol-based Ag/AgCl REs were investigated with respect to their stability and suitability for EIS. One contains $0.66 \text{ mol L}^{-1} \text{ H}_2\text{O}$ and one is completely water free. Both electrode types show a remarkable stability in their potential at 400 mV for a span of 49 days not deviating by more than 5 mV from the average of the first 14 days. The water in the RE compartment does not have a significant effect on the RE's impedances ($\sim 27 \text{ k}\Omega$). The relatively high impedances only cause small potential inaccuracies for DC measurements, and the REs are well suited for static protocols and reactions that do not require rapid potential adjustments. Between the water-containing and water-free Ag/AgCl REs, the latter is to be preferred in an anhydrous methanol cell electrolyte as it eliminates possible interdiffusion and cross contamination. However, the stability over 49 days for type 2 REs has to be verified as the potential of both prepared REs started to drop. The Ag/Ag⁺ REs proved stable for 14 days but drifted towards higher potentials afterwards. They show much lower impedances of $16 \text{ k}\Omega$, which results in a f_c of 2 MHz. Thus, it reacts faster to a changing reaction system than the Ag/AgCl REs. The impedance is low enough that they can be used for most standard EIS measurements, though it is still too large to be recommended for fast EIS measurements such as corrosion analysis behavior. The Ag wire provides the lowest impedance with only 80Ω but its half-wave potential is unreliable for longer measurements. Despite requiring the most maintenance, it is the most suitable RE among the ones tested for fast short-term EIS measurements and quickly changing reaction systems. For long-term EIS measurements ($>1 \text{ d}$), the Ag/Ag⁺ REs can be taken into account as a compromise between stability and low impedance. Note that the applied EIS frequency needs to be below the f_c as they are the highest possible frequencies in a simplified model calculation.

As only DC experiments were performed, the anhydrous Ag/AgCl REs were chosen to investigate electrode materials in an H-cell. The REs required minimal maintenance and avoided any possibility of water contamination of the anhydrous methanol electrolyte.

6 Electrochemical oxidation of anhydrous methanol in a batch H-cell

The previously developed methanolic Ag/AgCl RE can be used to investigate the methanol oxidation reaction (MOR) in a three electrode H-cell setup. Experimental conditions were adapted based on literature reports while using a modern RE for proof-of-concept investigations. Several transition metals were tested as anode materials. Because Pt was reported in the literature as an active material,^[34,36] it was also used to investigate the influence of the electrolyte concentration. All potentials are given vs Fc/Fc^+ , noted as vs Fc .

6.1 Investigation of anode materials

The electrooxidation of methanol to formaldehyde is highly influenced by the electrode material. Platinum was reported to be active for the formaldehyde formation.^[34–37] In addition, Cu, Ni, Ag, and Au are predicted to oxidize methanol via formaldehyde making them promising materials for the formaldehyde synthesis.^[99]

To investigate the activity of these five different electrode materials for the formaldehyde formation, CVs were measured with wire electrodes in 0.1 mol L^{-1} and 1.0 mol L^{-1} NaOMe and 0.1 mol L^{-1} NaClO₄. Different electrolytes and electrolyte concentrations were chosen to also account for possible interactions between the electrode and electrolyte. All supporting electrolytes are dissolved in pure methanol. The 10th CV cycle is shown unless otherwise noted. Whenever distinct oxidation peaks were observed, CAs were carried out at the peak potentials, and the product solution was analyzed for formaldehyde. Iwakura *et al.* reported CVs for Pt, Cu, Ni and Ag vs a

saturated calomel electrode (SCE) in 1.0 mol L^{-1} NaOMe, but only for Pt a product analysis was reported.^[36]

6.1.1 Platinum

Pt was tested to verify the literature reports on its activity for the methanol conversion to formaldehyde. The CV in 0.1 mol L^{-1} NaOMe and the CA, measured at the peak potentials of the CV, are shown in Figure 6.1. CVs in 1.0 mol L^{-1} NaOMe and in 0.1 mol L^{-1} NaClO₄ are shown in Figure A.2.

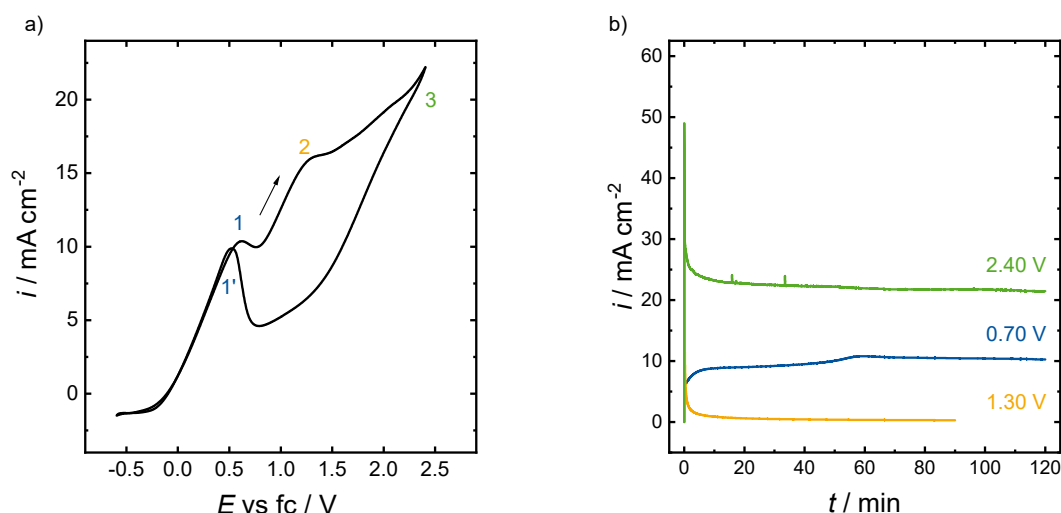


Figure 6.1: a) CV of a Pt wire in 0.1 mol L^{-1} NaOMe in MeOH with a scan rate of 100 mV s^{-1} . b) CA with the Pt wire at the peak potentials of the CVs for 2 h.

The CV curve shows two distinct oxidation peaks in the anodic sweep at 0.7 V and 1.3 V with peak current densities of 10.4 mA cm^{-2} and 16.1 mA cm^{-2} , respectively. The current response increases further with higher potentials to a maximum current density of 22.1 mA cm^{-2} at 2.4 V. An oxidation peak in the cathodic CV sweep roughly coincides with the first oxidation peak of the anodic sweep. The occurrence of multiple oxidation peaks indicates that different reactions occur at the different potentials.

The shape of the measured CV (Figure 6.1 a)) is similar to the methanol oxidation on Pt/C in aqueous media.^[179–181] The methanol CV of Pt/C shows an oxidation peak at 1 V vs RHE in the anodic sweep. With increasing potential the current response drops until it increases again at potentials above 1.2 V vs RHE. The CV also shows

an oxidation peak in the cathodic sweep, which is attributed to CO oxidation.^[181] In aqueous media, the oxidation peaks of the anodic and cathodic sweep do not overlap as the peak of the cathodic sweep is shifted to lower potentials.

Another potential-dependent factor that can influence CV shape is the Pt oxidation. In acidic aqueous electrolytes, elemental Pt is a highly active catalyst for the methanol oxidation at low potentials. With increasing potentials, Pt is then oxidized via PtO to PtO₂ at potentials above 1.05 V vs RHE.^[134] PtO₂ is a reportedly active catalyst for the methanol oxidation to formaldehyde in acidic electrolytes,^[32] though some reports say that it is less active than PtO, PtOH or Pt(OH)₂.^[136]

Chronoamperometry was conducted at the potential of each of the different oxidation peaks of the measured CV in 0.1 mol L⁻¹ NaOMe to investigate the potential dependent reaction products (Figure 6.1). HPLC analysis shows that formaldehyde was produced at all three potentials, but the amount of formaldehyde and the Faraday efficiency varies vastly (Table 6.1). The only liquid side product detected is formic acid.

Table 6.1: Yields, charge, product concentration and Faraday efficiencies for H-cell CAs in 0.1 mol L⁻¹ NaOMe. The yields have a an error of ± 3 mg.

E vs fc V	Charge C	$c(\text{CH}_2\text{O})$ mg L ⁻¹	$c(\text{CH}_2\text{O})$ mmol L ⁻¹	FE %
0.7	39.1	17	0.53	49
1.3	1.8	6	0.17	n.a.
2.4	88.0	71	6.20	78

At 0.7 V and 2.4 V, stable currents were achieved during the experiments. The comparison of the total charge and the formaldehyde yields lead to Faraday efficiencies of 49 % and 78 %, respectively. The measurement at 1.3 V was interrupted by the potentiostat due to the internal resistance of the system becoming too high. The calculated Faraday efficiency at this potential is beyond 100 %. This is ascribed to the low formaldehyde concentration, which is close to the detection limit of the HPLC. Hence, the HPLC analysis would lead to an exaggeration of the Faraday efficiency. The differing current responses and Faraday efficiencies also indicate that the applied potential influences the occurring reaction pathway. At 0.7 V, current was constantly flowing and even slightly increasing over the 2 h measurement. The increase in the internal resistance at 1.3 V might be caused by CO formation on the electrode surface, which is a known electrode poison on platinum.^[33] The measurement was interrupted after 90 min as no

more current was measurable. The highest applied potential of 2.4 V yields the highest Faraday efficiency and also the highest total current. The high Faraday efficiency suggests that formed formaldehyde is not subsequently oxidized to CO or CO₂, which could also have caused higher currents. The Faraday efficiencies obtained at 2.4 V are comparable to the ones described in the literature.^[34–37]

More recently, the reaction of pure methanol to formaldehyde in an electric field was predicted by Cassone *et al.* In a sufficiently strong electric field of 0.55 V Å^{−1}, methanol can theoretically disproportionate to formaldehyde, methane and water.^[182] No additional catalytic activity is required at these conditions. Such field strength can possibly be reached locally at the electrode-electrolyte interface.^[183] To investigate whether the proposed disproportionation is occurring, the water content was determined prior and after the CAs via a Karl Fischer coulometry (Table 6.2). The analysis shows that the water content remains nearly stable, while minor changes can also be caused by exchange with the atmosphere. According to the disproportionation by Cassone *et al.*, formaldehyde and water form in equal amounts.^[182] As the change in the water content is multiple orders of magnitude below the formation of formaldehyde, the disproportionation is not the dominant reaction mechanism. Hence, it is assumed that the detected formaldehyde forms during a catalytic conversion on the electrode surface.

Table 6.2: Comparison of the water content prior and after the CA measurements.

E vs Fc V	wt.% _{prior} (H ₂ O) -	wt.% _{after} (H ₂ O) -	$\Delta c(\text{H}_2\text{O})$ $\mu\text{mol L}^{-1}$
0.7	0.132	0.183	21.72
1.3	0.190	0.207	7.12
2.4	0.107	0.107	-

The CV was also performed in 1.0 mol L^{−1} NaOMe in MeOH (Figure A.2 a)) and in 0.1 mol L^{−1} NaClO₄ (Figure A.2 b)). In 1.0 mol L^{−1} NaOMe, higher current densities were reached but no cathodic oxidation peak was detected. In 0.1 mol L^{−1} NaClO₄, also higher current were measured and a second oxidation peak during the cathodic sweep. Because the measured CV peaks change with the electrolytes and its concentration, which indicates a strong dependency of the methanol oxidation on the electrolyte. A CV curve measured in 1.0 mol L^{−1} NaOMe was also reported by Iwakura *et al.*^[36] Their CV shape is similar to the one measured in this work, yet, a more detailed comparison is unfeasible due to incomplete documentation and different reference electrodes. The effects of the electrolyte are investigated in more detail in chapter 8.

Overall, Pt is active for the methanol oxidation in different supporting electrolytes. Faraday efficiencies of $>70\%$ and a high selectivity to formaldehyde can be achieved. Thus, it was investigated in more detail in a flow cell setup.

6.1.2 Copper

Cu was tested for the methanol oxidation to formaldehyde. A CV curve was reported but no information about the formed reaction products is available.^[36] The CV in 0.1 mol L^{-1} NaOMe (Figure 6.2) shows only minimal currents over the measured potential range. A small increase in the current density is observed at 0.9 V . Note that the wire slightly darkened throughout the CV measurement.

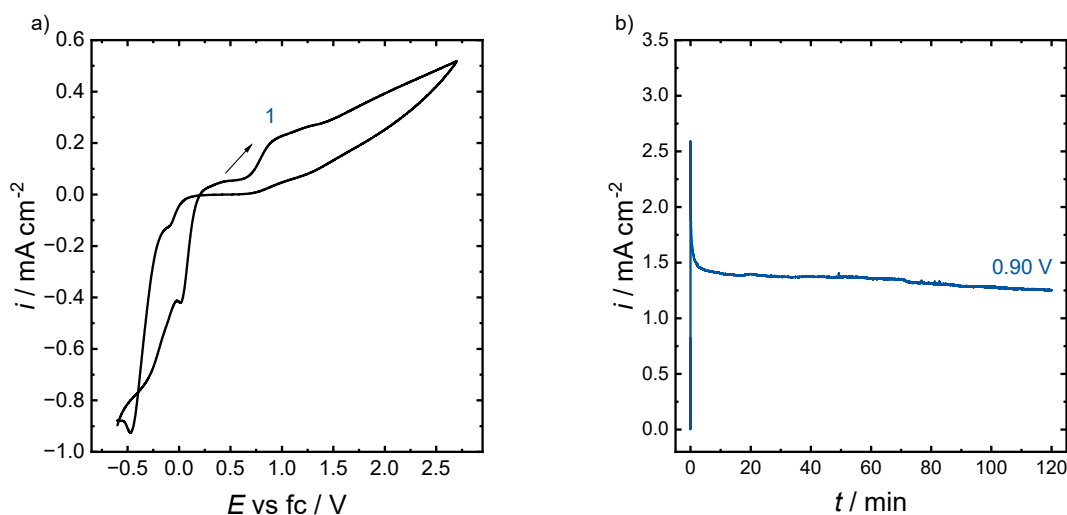


Figure 6.2: a) CV of a Cu wire in 0.1 mol L^{-1} NaOMe in MeOH with a scan rate of 100 mV s^{-1} . b) CA with the Cu wire at the peak potential of 0.9 V for 2 h.

The CV shows a distinct oxidation peak at 0.9 V and above the current response increases linearly with higher potentials. The darkening of the Cu wire can be an indication for the formation of CuO at higher potentials. Below 0.25 V , a reductive current was measured. The reduction of CuO back to Cu can contribute to the reductive current though the darkening increased with each cycle as it was not fully reversed during the reductive sweep. The reductive processes were not investigated in more detail as the focus was on the methanol oxidation.

A CA was carried out at 0.9 V for 2 h to investigate whether any formaldehyde formation occurs (Figure 6.2 b)). The current density received was slightly below 1.5 mA cm^{-2}

at the end of the experiment. It is noteworthy that the CA current is above the CV current at the same potential. After the CA, a formaldehyde concentration of 22 mg L^{-1} was found in solution, which is more than what was detected for the Pt electrode at 0.7 V . The formaldehyde concentration determined for Cu equals a Faraday efficiency of 187% . The low formaldehyde concentration is near the detection limit of the HPLC, which inflates measurement inaccuracies.

CVs were also measured in $1.0 \text{ mol L}^{-1} \text{ NaOMe}$ and $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$ (Figure A.3). Here, the CV curve measured in $1.0 \text{ mol L}^{-1} \text{ NaOMe}$ differs from the one measured in $0.1 \text{ mol L}^{-1} \text{ NaOMe}$ showing a clear peak which current response decreased with each cycle and shifted to lower potentials. This CV shape does not match the one reported by Iwakura *et al.*^[36] In NaClO_4 , dissolution of the Cu wire was observed above 1.0 V (Figure A.3 b)). Because of the low current response, Cu seems to be rather inactive for the methanol oxidation. Because of the increasing oxidation in NaOMe and dissolution in NaClO_4 , it cannot be assumed to be a stable electrode material. Thus, it was not investigated further as a potential anode material. It might be worth investigating a CuO electrode.

6.1.3 Nickel

The CV curve of Ni measured in $0.1 \text{ mol L}^{-1} \text{ NaOMe}$ is shown in Figure 6.3 a). The current sharply increases in the anodic sweep from 0 mA cm^{-2} at 0.8 V to 14 mA cm^{-2} at 1.8 V . The current then slightly drops before it starts rising again at potentials over 2.3 V . The Ni wire changed to a dull, dark gray color at potentials around 1.12 V in all tested electrolytes. The coloration vanished during the cathodic sweep. In the cathodic sweep, there is a current peak at 1.4 V . The highest overall current was measured at the highest potential of 2.5 V . These three potentials were chosen for CA measurements (Figure 6.3 b)). At 1.12 V , the current response is close to 0 mA cm^{-2} , which indicates that only the anode is oxidized. When the applied potential is increased to 1.4 V , a steady current density is measured around 5 mA cm^{-2} , while the CA at 2.5 V resulted in the highest current density, which was stable at 13 mA cm^{-2} but noisy. The latter CA was repeated to exclude an experimental setup error. The measured current density was less noisy but it dropped from 17 mA cm^{-2} after 5 min to 8 mA cm^{-2} after 2 h . The differences in these two curves indicate that the Ni-electrolyte interface is not stable and potentially multiple redox reactions occur.

A product analysis of the CA at 2.5 V after 2 h yielded a formaldehyde concentration

of 108 mg L^{-1} and a formic acid concentration of 61 mg L^{-1} . These concentrations correspond to 121 % Faraday efficiency for formaldehyde and 89 % for formic acid. The Ni dissolution during the CA might have caused inaccuracies in the HPLC, which is sensitive to metal ions.

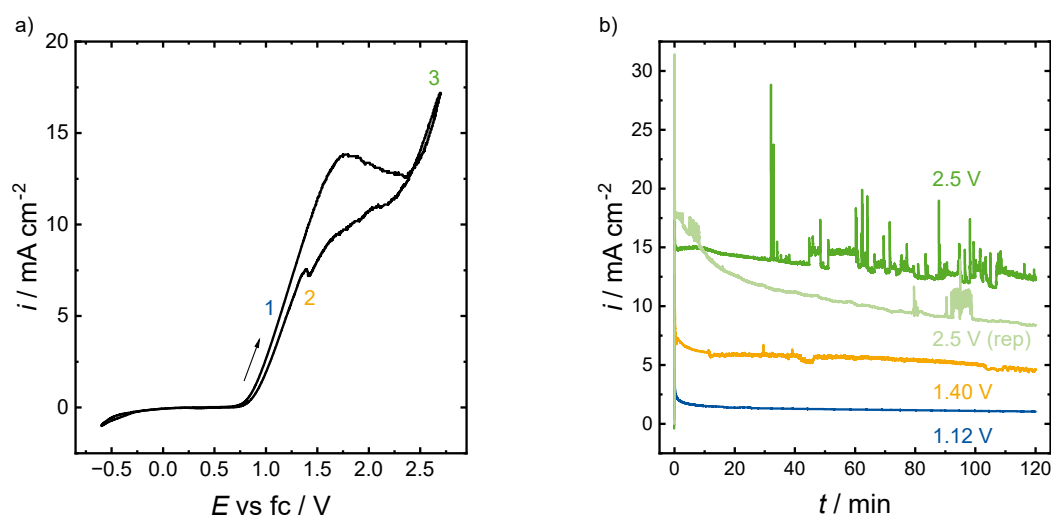


Figure 6.3: a) CV of a Ni wire in 0.1 mol L^{-1} NaOMe in MeOH with a scan rate of 100 mV s^{-1} . b) CA with the Ni wire at the peak potentials of the CVs for 2 h. The first potential was chosen because of the anode color change.

CVs of Ni were also measured in 1.0 mol L^{-1} NaOMe and 0.1 mol L^{-1} NaClO₄ (Figure A.4). The CV in 1.0 mol L^{-1} NaOMe shows no current response until it sharply increases at potentials over 0.9 V. Other peaks are not observed. The shape of the CV is in accordance with literature.^[36] The CV in 0.1 mol L^{-1} NaClO₄ has a similar shape to the one in 1.0 mol L^{-1} NaOMe, but the current increases at potentials above 1.9 V. The discrepancy of the CV curves in the different electrolytes indicates an electrolyte sensitivity of Ni for the methanol oxidation reaction. Because of the high current response also at low potentials in NaOMe, a more in-depth investigation of Ni as anode material was continued in a flow cell setup.

6.1.4 Silver

A Ag wire as the anode was also tested in different electrolytes in the H-cell setup. The CV measured in 0.1 mol L^{-1} NaOMe is shown in Figure 6.4 a). During the anodic sweep, the curve has an oxidation peak at 0.88 V of 3 mA cm^{-2} . Afterwards, the current

density drops and then starts to increase again at potentials over 1.2 V. The maximum current is reached at 2.4 V with 7 mA cm^{-2} . The CV also shows a significant reductive current peak during the cathodic sweep at 0.17 V. Its peak current is the largest measured during the CV with -13 mA cm^{-2} . The color of the Ag wire changed between metallic Ag and matte black, which indicates that at least some current is used in the oxidation and reduction of the electrode.

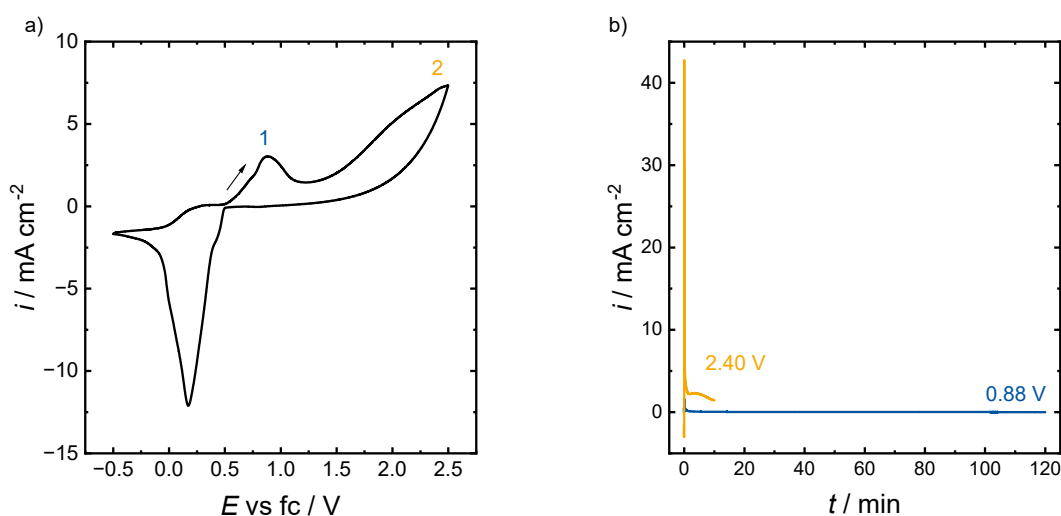


Figure 6.4: a) CV of a Ag wire in 0.1 mol L^{-1} NaOMe in MeOH with a scan rate of 100 mV s^{-1} . b) CA with the Ag wire at the peak potentials of the CVs for 2 h.

A CA was carried out at the two CV peak potentials of the anodic sweep (0.88 V, 2.4 V, Figure 6.4 b)). At 0.88 V, no significant current flow was observed. After an initial peak, the current drops to 0. A gray layer formed on top of the Ag wire, which is most likely Ag_2O . The CA with 2.4 V was stopped after a few minutes as the Ag wire was completely oxidized to Ag oxide and dark flakes were suspended into solution. An HPLC analysis of the 0.88 V CA showed that a formaldehyde concentration of 14 mg L^{-1} was obtained, which equals a Faraday efficiency of 7 %.

CVs of the Ag wire were also measured in 1.0 mol L^{-1} NaOMe and 0.1 mol L^{-1} LiClO_4 (Figure A.5). Note that the other materials were measured in NaClO_4 . The CV shape in 1.0 mol L^{-1} NaOMe matches the one reported by Iwakura *et al.*^[36] The CV in LiClO_4 shows no distinct oxidation peaks in the anodic sweep (Figure A.5 b)). At potentials above 1 V, the current response increases sharply. At these potentials, the Ag wire was not stable in LiClO_4 , which allowed only 5 complete CV cycles to be measured. Thus, it was not investigated further as an anode material.

6.1.5 Gold

Au is predicted to be active for the methanol oxidation and was, therefore, also investigated as anode material.^[98,99] The CV of a Au wire in 0.1 mol L⁻¹ NaOMe is shown in Figure 6.5 a). Three distinct peaks are visible in the anodic sweep at 0.69 V with 14 mA cm⁻², 1.12 V with 17 mA cm⁻², and at 2.5 V with 19 mA cm⁻². In the cathodic sweep, there is an additional oxidative current peak at 0.48 V with 2 mA cm⁻² with a shoulder at 0.23 V (0.3 mA cm⁻²) and a reductive current peak at 0.04 V with -2 mA cm⁻². The CV curve resembles the one measured for Pt. CAs were measured at each of the three potentials of the anodic sweep (Figure 6.5 b)).

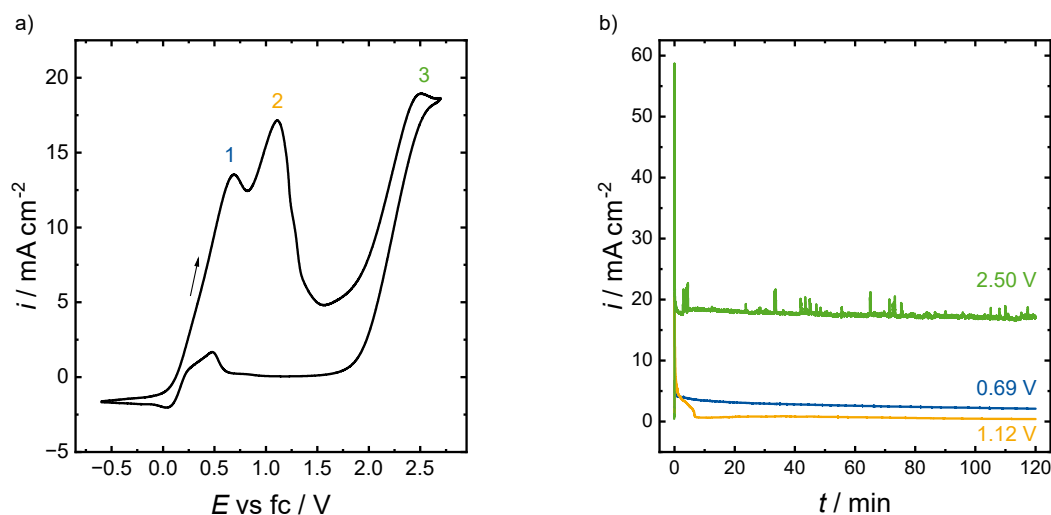


Figure 6.5: a) CV of a Au wire in 0.1 mol L⁻¹ NaOMe in MeOH with a scan rate of 100 mV s⁻¹. b) CA with the Au wire at the peak potentials of the CVs for 2 h.

The CA at 0.69 V results in a current density of 4 mA cm⁻² after 2 h. A similar behavior was observed for the CA with 1.12 V applied, which exhibits a current density of 2 mA cm⁻². Despite well defined current peaks during the CVs, little methanol was oxidized and neither formaldehyde nor formic acid were detected via HPLC. Instead, it is possible that CO or CO₂ formed. At 2.5 V, a current density of 17 mA cm⁻² was measured at the end of the CA. HPLC analysis shows a formaldehyde concentration of 67 mg L⁻¹, which equals a Faraday efficiency of 92 %. A concentration of formic acid was obtained of 29 mg L⁻¹. This equals a Faraday efficiency of 52 % for formic acid resulting in a total Faraday efficiency of over 100 %. On overestimation of the individual concentrations is likely caused by peak overlapping in the HPLC detection.

The CV in 1.0 mol L^{-1} NaOMe (Figure A.6 a)) is similar in shape to the one measured in 0.1 mol L^{-1} NaOMe but it is shifted by 0.2-0.3 V to lower potentials. In 0.1 mol L^{-1} NaClO₄ (Figure A.6 b)), the CV curve differs from the ones measured in NaOMe as there is only one oxidation peak observed in the anodic sweep. This indicates that different reaction pathways occur in the perchlorate electrolyte compared to the methoxide ones. The electrolyte influence was investigated further in chapter 9. The Au wire anode produces formaldehyde in high amounts with a high selectivity and thus, it was chosen to investigate Au as the anode material in the flow cell.

In summary, Pt, Ni and Au show promising activity and stability for the methanol oxidation in the H-cell. These materials are tested in a flow cell setup to evaluate their performance on a larger scale and at elevated current densities in chapter 7.

6.2 Influence of the electrolyte concentration

The electrolyte concentration directly influences reaction parameters such as the electrolyte basicity, viscosity, and conductivity. To investigate whether these factors influence the methanol oxidation, CAs were conducted with a Pt wire WE. Pt was chosen as it showed the highest activity for the formaldehyde synthesis based on the previously conducted material screening. Methanolic NaOMe was the electrolyte of choice that was measured in 0.1 mol L^{-1} , 0.5 mol L^{-1} , and 1.0 mol L^{-1} and the CA curves are shown in Figure A.7. The Faraday efficiencies and the total amounts of produced formaldehyde are shown in Figure 6.6.

The Faraday efficiency decreases from 78 % to 50 % with increasing electrolyte concentration, whereas the overall formaldehyde yield increases from 71 mg L^{-1} (0.1 mol L^{-1}) to 199 mg L^{-1} and 176 mg L^{-1} for 0.5 mol L^{-1} and 1.0 mol L^{-1} NaOMe, respectively. The larger yields are a result of the higher currents that flowed at higher electrolyte concentrations. The transferred charge increase from 88 C to 345 C from 0.1 mol L^{-1} to 0.5 mol L^{-1} and to 400 C for 1.0 mol L^{-1} . This indicates that the higher conductivity for the more concentrated electrolytes. The larger amounts of produced formic acid in the 1.0 mol L^{-1} electrolyte lower the Faraday efficiency. The exact concentrations for formaldehyde and formic acid are shown in Table A.11.

These results show that the methanol oxidation is sensitive to the electrolyte composition and concentration. Thus, the effects of the electrolyte composition and supporting electrolyte concentration are investigated in the flow cell to understand how they affect the methanol oxidation in a larger setup (chapter 8).

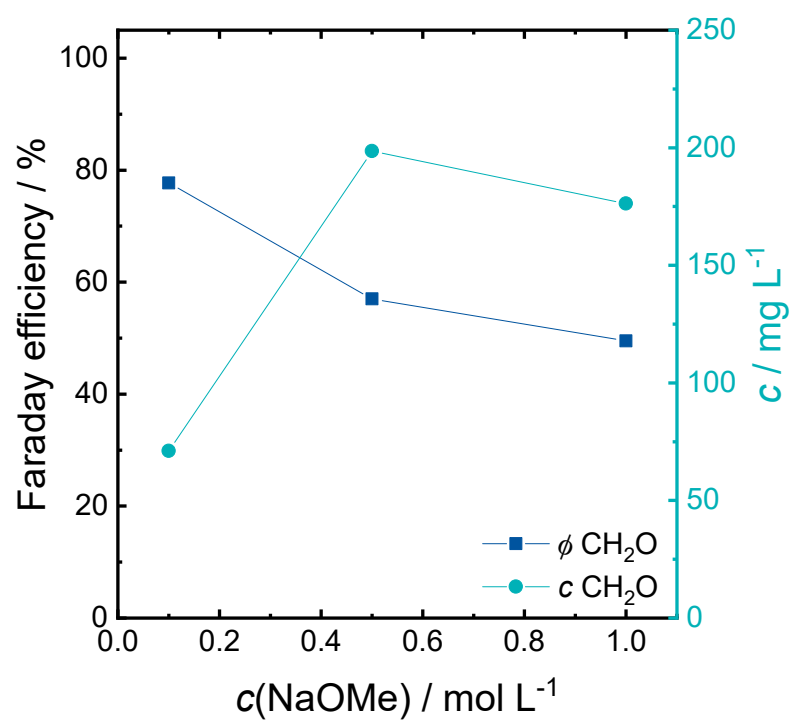


Figure 6.6: Faraday efficiency (ϕ) and concentration of produced formaldehyde at different NaOMe concentrations in a H-cell on a Pt working electrode after a 2 h CA at 2.4 V.

7 Impact of the scale-up and flow cell parameters on the formaldehyde formation

After the successful study of the anhydrous formaldehyde synthesis from methanol on a small scale, the methanol oxidation was transitioned to a flow cell setup. The influence of the setup was systematically investigated to analyze the scalability of the reaction for potential industrial application. In the flow cell, the electrode size increased to 12 cm^2 and the electrolyte flows over the electrodes.

A major difference between the H-cell and the flow cell is the mode of operation. In the H-cell, a 3 electrode setup was used and a constant potential was applied. In the flow cell, only two electrodes were used and a constant current flow was set in the potentiostat while the potential was measured. The cathode was a Pt coated titanium plate (Pt/Ti) with a surface area of 25 cm^2 for all experiments.

7.1 Measurement reproducibility

As a flow cell contains numerous variable parameters, the reproducibility of the setup and the reaction was investigated. The same experimental series was repeated a total of five times by three different experimenters over an extended period of time. The current was stepwise increased from $10\text{--}100\text{ mA cm}^{-2}$ on a 12 cm^2 Pt electrode. The electrolyte consisted of 40 mL of 0.1 mol L^{-1} NaClO_4 in methanol. The Faraday efficiencies for formaldehyde are shown in Figure 7.1.

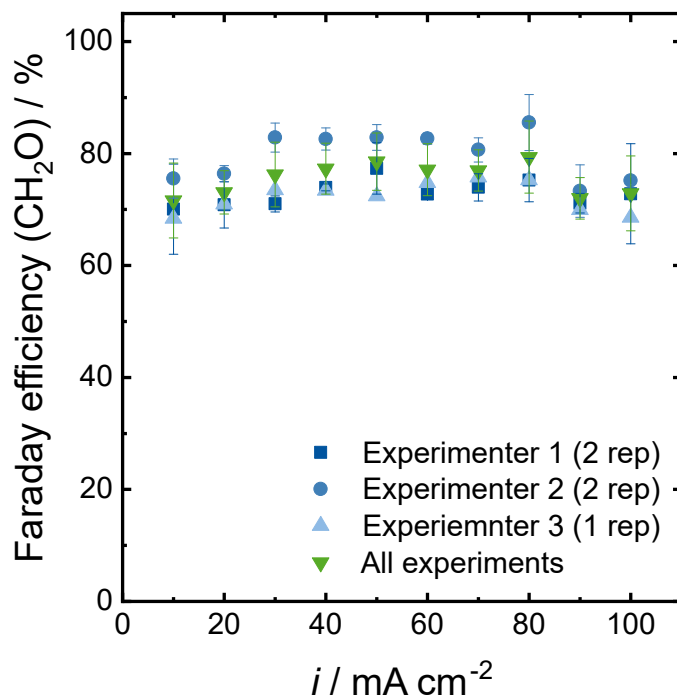


Figure 7.1: Faraday efficiency for formaldehyde on Pt in 0.1 mol L⁻¹ NaClO₄ between 10-100 mA cm⁻². The measurements were carried out by three different persons at different times (blue). The measurement was repeated a total of five times (green).

Experimenter 1 measured the series twice (Figure 7.1, dark blue) with Faraday efficiencies between 70-75 % for all applied current densities with an average standard deviation of 3.5 %. These results are in good agreement with the Faraday efficiencies measured by Experimenter 3 (Figure 7.1, light blue). Here, the Faraday efficiencies range between 68-76 %. Experimenter 2 repeated the series twice with Faraday efficiencies between 73-86 % and an average standard deviation of 2.5 %. These Faraday efficiencies are considerably higher than the ones measured by Experimenter 1 and 3. The average of all 5 experiments (Figure 7.1, green) shows an average standard deviation of 5 %. Each individual series is in better agreement with itself, but also other effects need to be taken into account. Among others, process parameters such as changing room temperature during the year might impact the Faraday efficiency. Furthermore, these difference in Faraday efficiency can also be caused by aging of the cell gaskets or the HPLC column.

Overall, an uncertainty of up to 5 % needs to be taken into account when comparing measurements from carious experiments or reproducing any of the presented results using the flow cell setup.

7.2 Anode material

In the H-cell setup, different transition metals were tested as anode materials for the methanol oxidation to formaldehyde. Among those, Pt, Ni and Au showed reasonable activity for the methanol oxidation. These elements were tested in the flow cell with 12 cm^2 surface areas in 0.1 mol L^{-1} NaOMe. Chronoamperometries were performed with current densities from $10\text{--}100\text{ mA cm}^{-2}$ with duration of 30 min each. The Faraday efficiencies were calculated to evaluate the electrode's performance.

7.2.1 Platinum

In the H-cell, Faraday efficiencies for formaldehyde on a Pt anode of up to 78 % were measured. In the flow cell, the Faraday efficiencies are between 79 % and 93 % (Figure 7.2). A steady increase in Faraday efficiency is observed from $10\text{--}60\text{ mA cm}^{-2}$ with a slight decrease afterwards. The Faraday efficiency for formic acid decreases from 9 % at 10 mA cm^{-2} to 2 % at 100 mA cm^{-2} . This indicates a kinetic limitation of the formic acid formation across the different current densities, which will be discussed in more detail in chapter 8. The Faraday efficiencies at elevated current densities in the flow cell are higher compared to the H-cell experiments. The introduction of mass transport by an electrolyte flow seems to benefit the formation of formaldehyde as it reduces the contact time with the electrodes. This matches the findings reported by Haisch *et al.* who reported a beneficial correlation between the formaldehyde formation and the mass transport in an aqueous alkaline electrolyte.^[31] A more in-depth study of the influence of the flow rate is described in section 7.4.

With no other detected liquid side products, $\sim 10\%$ of the Faraday efficiency remains unaccounted for. This could possibly be attributed to further oxidation of formaldehyde and formic acid to CO and CO₂, respectively. An analysis of the gas phase of the reaction by GC shows it consists of 49 % hydrogen, 10 % air, 1 % CO and 0.1 % CO₂. There was an additional unidentified peak after 12 min, which could be caused by methanol or formaldehyde. The detected air signal is an indicator that the setup was not completely tight. Some of the formed gasses may also be dissolved in the electrolyte and thus, not be detected via the GC analysis. The Faraday efficiency can also decrease due to the reduction reactions of formaldehyde and formic acid. On the cathode, the main counter reaction is the hydrogen evolution reaction (HER). If, e.g., formaldehyde comes in contact with the cathode, hydrogen is present as well as a re-

ductive potential. As Pt is active for the oxidation reaction with in oxidative potential, it can also facilitate the reduction reaction when a reductive potential is applied. This can be avoided by using another cathode material or introduce a separator in the flow cell.

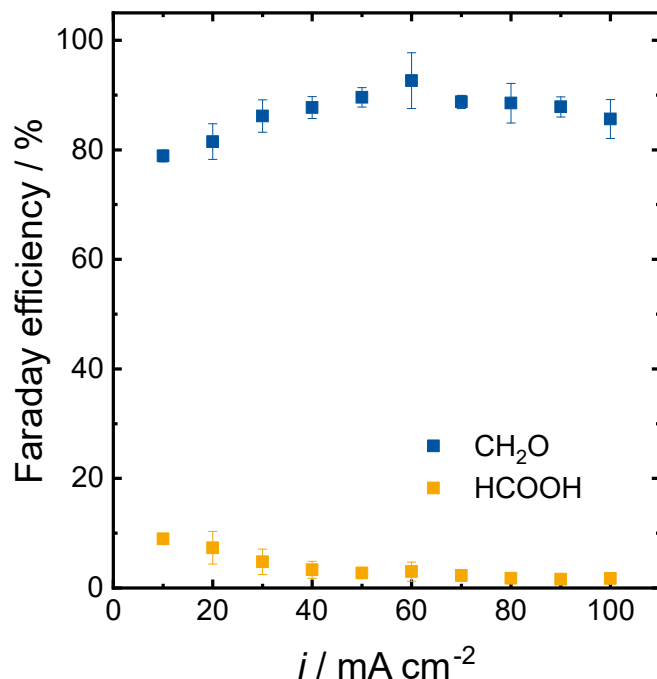


Figure 7.2: Faraday efficiency for formaldehyde (blue) and formic acid (orange) on a Pt foil in $0.1 \text{ mol L}^{-1} \text{ NaOMe}$ as a function of the current density. The measurements were performed at RT for 30 min with an electrolyte volume of 40 mL and a flow rate of 100 mL min^{-1} . The experimental series was measured three times and the standard deviation is shown as error bars.

Pt shows a high activity for the methanol oxidation and a high selectivity to formaldehyde. It also appears stable at higher current densities. Both properties are crucial for further scale-up and possible industrial application.

7.2.2 Nickel

Because of a coloration of the electrolyte to light green, Ni was exclusively evaluated at low current densities between $10\text{--}30 \text{ mA cm}^{-2}$. The respective CPs are shown in Figure 7.3. At 10 mA cm^{-2} , a constant potential of 3.95 V was measured. At higher

current densities, the potential starts drifting to higher values. The green coloration of the solution suggests the formation of nickel formate ($\text{Ni}(\text{HCOO})_2$).^[184]

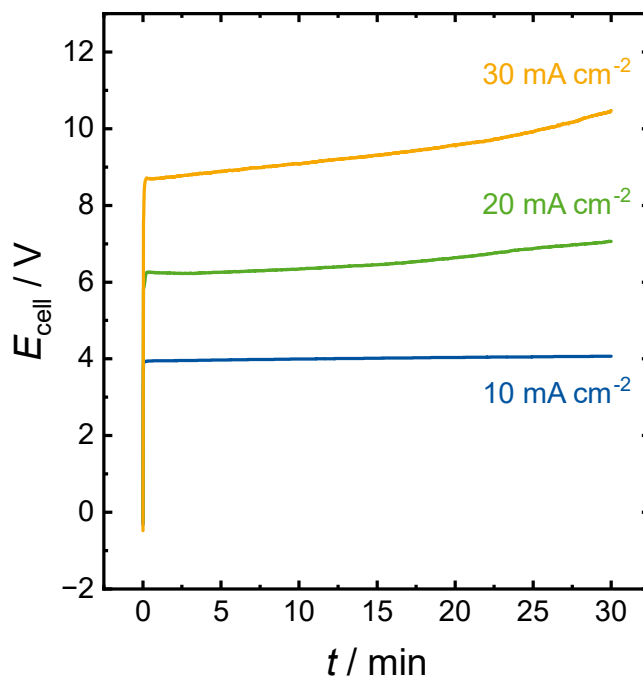


Figure 7.3: Cell potentials as a function of the time for the Ni anode CPs. The measurements were performed at RT for 30 min in 40 mL 0.1 mol L^{-1} NaOMe with a flow rate of 100 mL min^{-1} .

The samples were not measured via HPLC as the used column is sensitive towards dissolved metal ions. Thus, a direct comparison with the other materials is not possible as no Faraday efficiency could be calculated. Ni proves unstable at higher current densities in methanol and was, thus, not investigated further.

7.2.3 Gold

In the H-cell, a Faraday efficiency of 92 % for formaldehyde and 52 % for formic acid were measured. Conversely, formic acid was the main product with Faraday efficiencies between 51-58 % (Figure 7.4) in the flow cell. The highest Faraday efficiency to formaldehyde was at 10 mA cm^{-2} with 52 % and decreasing constantly to 37 % at 100 mA cm^{-2} . This downward trend in the Faraday efficiency is also observed for formic

acid with increasing current densities. The Au foil also darkened after applying high potentials suggesting that some Au dissolution occurred during the experiments.

The promising results from the H-cell experiments were not confirmed in the larger flow cell setup with the instability of the Au anode in methanol and formic acid being the main product. Thus, Pt was chosen as the anode material for further investigations.

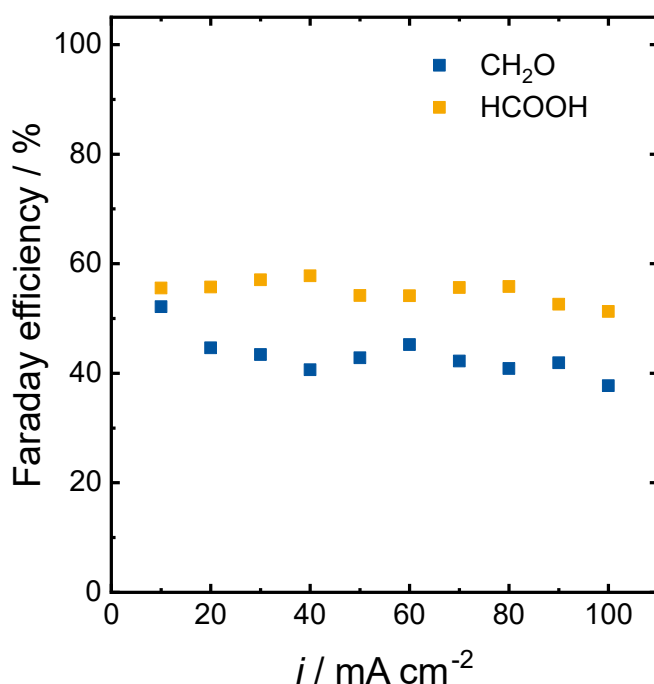


Figure 7.4: Faraday efficiency for formaldehyde (blue) and formic acid (orange) on a Au foil in 0.1 mol L^{-1} NaOMe as a function of the current density. The measurements were performed at RT for 30 min with an electrolyte volume of 40 mL with a flow rate of 100 mL min^{-1} .

7.3 Variation of the platinum anode support

In aqueous methanol solutions, it was reported that smooth surfaces favor the formation of formaldehyde while rough surfaces enable further oxidized products.^[26,128,135] Isolated Pt atoms also favor the partial oxidation of methanol.^[138] To investigate the effect of the electrode structure on the reaction performance, different Pt surfaces and electrode modifications were studied.

7.3.1 Platinum on titanium

Previous experiments were carried out with a pure Pt foil. SEM images shows that the Pt surface is smooth (Figure 7.5 a)). For a more efficient material usage, Pt deposited on a Ti sheet (Pt/Ti) was tested as the anode. The surface of the deposited Pt is composed of spherical grains that create an uneven structure with mounds and valleys (Figure 7.5 b)). The Pt spheres have an average diameter of 2-3 μm .

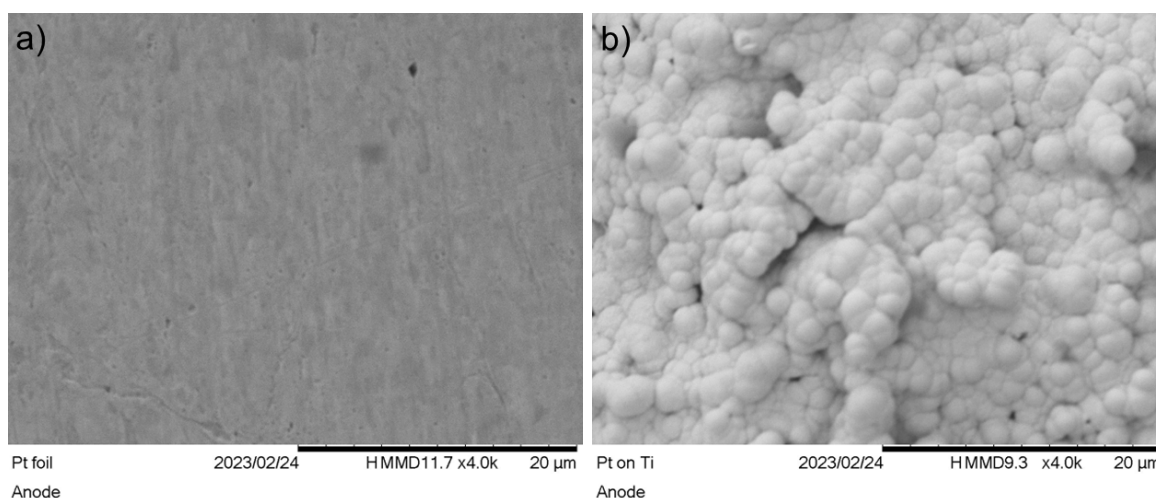


Figure 7.5: SEM images of the a) a Pt foil and b) a Pt/Ti electrode taken at magnifications of 4000.

To compare the effect of the surface structure, a CP series with identical parameters were run with both electrodes in 0.1 mol L^{-1} NaOMe in methanol. The Faraday efficiencies of the Pt foil are shown in Figure 7.6 in gray as reference. The Faraday efficiencies for formaldehyde are slightly lower for Pt/Ti compared to the Pt foil. In contrast, a slightly higher amount of formic acid is produced. The trends for both electrodes are similar with a higher Faraday efficiency for formaldehyde and a lower one for formic acid with increasing current densities. These results agree with the literature in which a rough surface allows more side reactions due to more available Pt sites.^[26,33,128,135,138] A rough surface also slows the mass transport near the surface because of the formation of channels and pockets in which only diffusion occurs.

To further investigate the influence of the electrode size, the surface area of Pt/Ti, initially limited to 12 cm^2 , was enlarged. Experiments with 25 cm^2 Pt/Ti electrodes were conducted with the previously described reaction conditions. The Faraday efficiencies for the 25 cm^2 Pt/Ti electrode are shown in Figure 7.7 with the 12 cm^2 Pt/Ti electrode for reference. The Faraday efficiencies for both, formaldehyde and formic

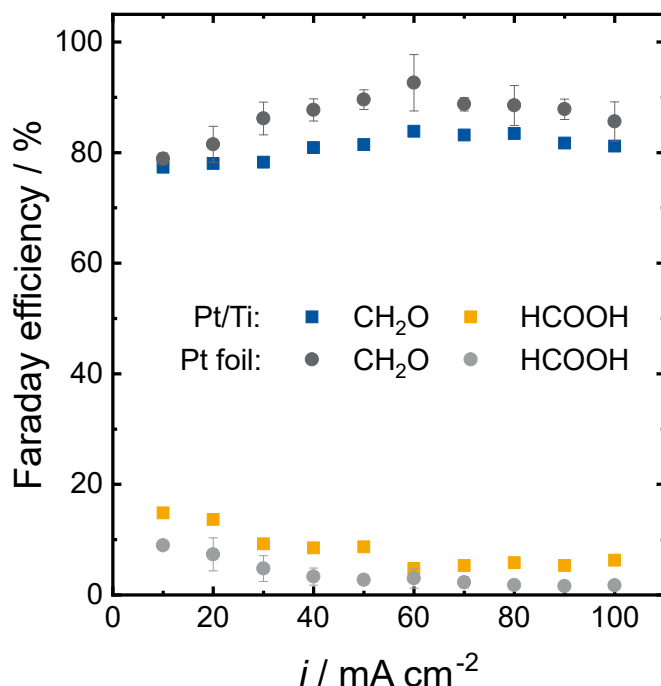


Figure 7.6: Comparison of the Faraday efficiencies for the methanol oxidation with Pt/Ti for formaldehyde (blue) and formic acid (orange). The Faraday efficiencies for the smooth Pt foil are shown for reference (gray).

acid, differ by 2-3 % for both electrode sizes for current densities of 10-50 mA cm^{-2} . At 60-70 mA cm^{-2} , the Faraday efficiency for formaldehyde for the larger electrode is 5 % lower compared to the 12 cm^2 electrode. Yet, both series are mostly within the flow cell reproducibility error. Note that the experiments with a 25 cm^2 anode were only conducted once. Higher current densities ($>70 \text{ mA cm}^{-2}$) were not possible as the compliance limit voltage (20 V) of the potentiostat was reached. At low current densities, the obtained formaldehyde concentration scales linearly with the electrode size. The ratio of the formaldehyde concentrations for both electrode sizes is 2.08 at 10 mA cm^{-2} , which is the same ratio by which the electrode size is increased from 12 cm^2 to 25 cm^2 . However, the ratio of the formaldehyde concentration decreases with increasing current densities to 1.95 at 70 mA cm^{-2} . The decreasing Faraday efficiency may be a result of subsequent formaldehyde reactions when the product concentration becomes too large as the formaldehyde concentration of the large electrode at 50 mA cm^{-2} surpasses the one obtained at 100 mA cm^{-2} for the small electrode. The effect of the formaldehyde concentration on the Faraday efficiency is investigated in more detail in section 8.6.

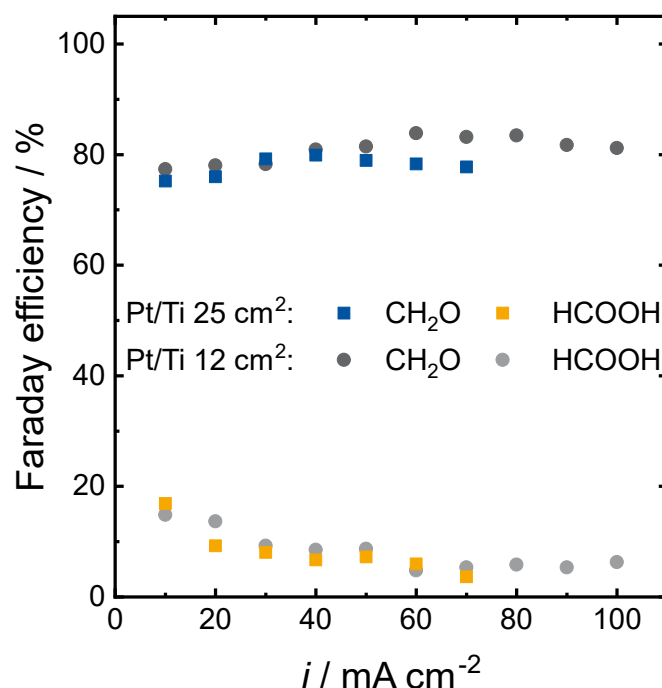


Figure 7.7: Scale-up of a Pt/Ti anode from 12 cm² (Faraday efficiencies shown in gray) to 25 cm². Faraday efficiencies shown in blue for formaldehyde and orange for formic acid.

7.3.2 Platinum on carbon gas diffusion electrode

In aqueous acidic electrolytes, small Pt centers are beneficial for the formaldehyde formation, while larger ones enable further oxidation.^[138] A porous structure with finely dispersed Pt particles can, thus, potentially increase the active surface area of Pt while maintaining a high selectivity. Pt/C gas diffusion electrodes (GDEs) are commercially available for fuel cell applications. Their use also has the advantage to be easily integrated into a membrane electrode assembly to minimize the electrode gap. A pure carbon cloth and a carbon GDE with 0.5 mg cm⁻² Pt loading were tested for their performance in methanol oxidation. The Pt foil was still used as a connector between the current collector and the carbon cloth/ Pt/C GDE, which were set on top of the Pt foil. The Faraday efficiencies of both carbon structures are shown in Figure 7.8 with the pure Pt foil as reference.

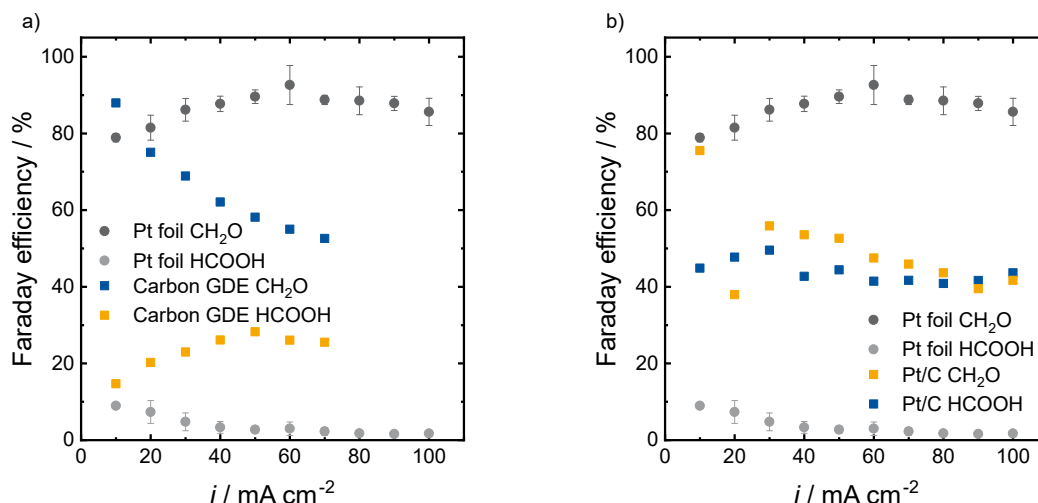


Figure 7.8: Faraday efficiency for formaldehyde (blue) and formic acid (orange) for a) a pure carbon cloth and b) a Pt/C GDE, which were set on top of the Pt foil. The Faraday efficiencies obtained with just the Pt foil are shown in grey. The CPs were measured in 0.1 mol L^{-1} NaOMe in MeOH for 30 min with 12 cm^2 electrodes.

Figure 7.8 a) shows the performance of the carbon cloth. The Faraday efficiency for formaldehyde drops significantly with each current step from 88 % at 10 mA cm^{-2} to 53 % at 70 mA cm^{-2} . The Faraday efficiency for formic acid increases from 15 % to 28 %. For the reaction to occur, methanol need to migrate through the carbon structure to reach the active site, and afterwards, formaldehyde needs to leave the electrode and move to the electrolyte bulk phase. Both processes are much slower due to the carbon cloth than the introduced mass transport by the electrolyte flow. The slow product removal from the electrode surface increases the possibility of subsequent oxidation reactions. The measurement was not carried out at higher current densities ($>70 \text{ mA cm}^{-2}$) because the carbon cloth showed visible degradation in form of particle detachment.

The Pt/C GDE shows a higher selectivity to formic acid than to formaldehyde (Figure 7.8 b)). The Faraday efficiency for formaldehyde ranges from 41 % to 50 %, whereas the Faraday efficiency for formic acid starts at 76 % at 10 mA cm^{-2} and drops to 40 % at 100 mA cm^{-2} . Similar to the carbon cloth, the Pt/C GDE slows down the mass transport near the active sites. Formaldehyde can form on the active sides of the Pt/C GDE or the Pt foil. Upon desorption, formaldehyde migrates towards the bulk phase. But as long as it remains in the Pt/C GDE, formaldehyde may get oxidized to formic acid in contact with other Pt particles. The required oxygen may be provided by existing oxygen groups on the carbon surface.

Overall, introducing carbon structures to the electrode surface lowered the Faraday efficiencies for formaldehyde. Even though the active area was increased by using a Pt/C GDE, the performance decreased indicating that a fast mass transport on the electrode surface is crucial for a high formaldehyde production.

7.4 Variation of flow rates

The experiments with the carbon cloth structures as anode support suggest that a fast mass transport near the electrode surface is beneficial for the formaldehyde formation. This was also reported for the oxidation of aqueous formaldehyde,^[26] but it has not been studied for the anhydrous methanol oxidation. The mass transport depends on the reactor design, the flow rate and the electrolyte properties. The reactor design (flow cell) was kept constant for these experiments. The flow rate was varied for two different NaOMe concentrations at 3 mA cm^{-2} (Figure 7.9) and 100 mA cm^{-2} (Figure 7.10) to investigate the influence of the flow rate.

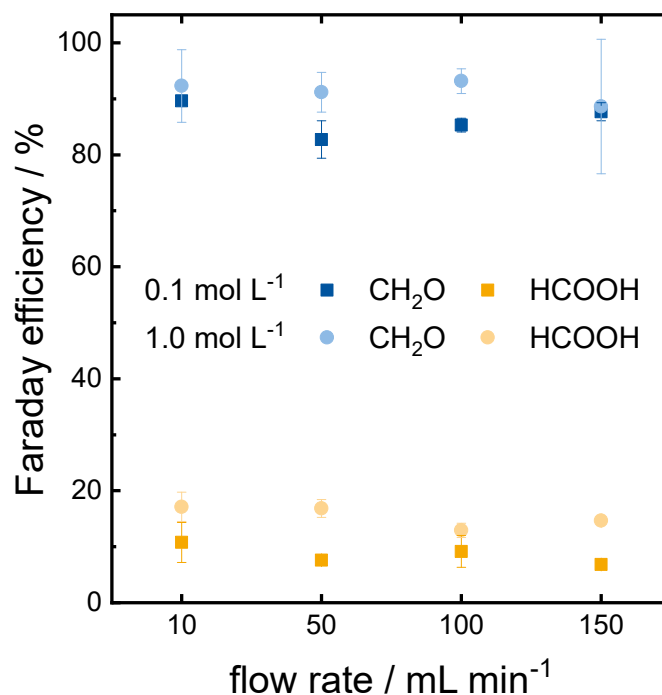


Figure 7.9: Faraday efficiency of formaldehyde and formic acid at different NaOMe concentrations and flow rates on Pt after 30 min CP at 3 mA cm^{-2} .

The Faraday efficiencies in 0.1 mol L^{-1} NaOMe vary between 84-89 % for formaldehyde and 7-11 % for formic acid being almost constant ($\pm 5 \%$) across different flow rates. At low current densities, the use of 1.0 mol L^{-1} NaOMe hardly affects the Faraday efficiencies. The constancy of the Faraday efficiencies across different flow rates and the negligible effect of the electrolytes viscosity suggest that the mass transport is not the limiting factor at low current densities. At higher current densities of 100 mA cm^{-2} , an influence of the flow rate on the formaldehyde formation is observed (Figure 7.10).

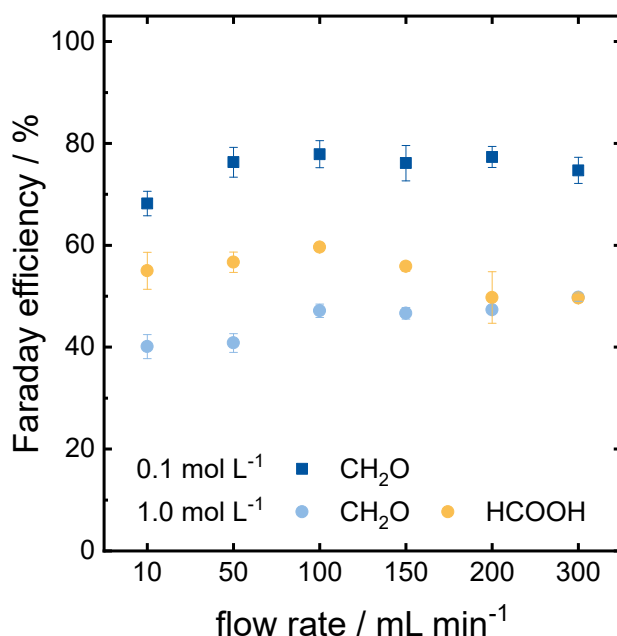


Figure 7.10: Faraday efficiency of formaldehyde and formic acid at different NaOMe concentrations and flow rates on Pt after 30 min CP at 100 mA cm^{-2} .

In 0.1 mol L^{-1} , the lowest Faraday efficiency for formaldehyde was 68 % at 10 mL min^{-1} (Figure 7.10 dark blue). Between $50\text{--}300 \text{ mL min}^{-1}$, the Faraday efficiency was constant around 76 %. No formic acid was detected. This indicates that the reaction occurs independent of the mass transport at flow rates $\geq 50 \text{ mL min}^{-1}$. The lower Faraday efficiency at the low flow rate might be caused by a longer retention time near the electrode surface, which allows subsequent oxidation. Formic acid formed in small amounts ($\leq 2 \%$ Faraday efficiency) as there is a non-quantifiable peak shoulder visible in the HPLC.

In 1.0 mol L^{-1} , the Faraday efficiency for formaldehyde increases from 40 % to 50 % when the flow rate is increased from 10 mL min^{-1} to 300 mL min^{-1} (Figure 7.10 light blue). In contrast to 0.1 mol L^{-1} NaOMe, formic acid was produced with Faraday ef-

efficiencies of up to 60 % at 100 mL min^{-1} . At higher flow rates, the Faraday efficiency for formic acid slightly decreases to 50 % at 300 mL min^{-1} . Conversely to the diluted electrolyte, the Faraday efficiencies for formaldehyde in 1.0 mol L^{-1} NaOMe increase with higher flow rates.

The Faraday efficiencies were also determined at 20 mL min^{-1} and 100 mL min^{-1} for 0.1 mol L^{-1} NaOMe (Figure A.8) and NaClO_4 (Figure A.9) at current densities ranging from 10 – 100 mA cm^{-2} . At low current densities, the flow rate does not impact seem to impact the formaldehyde formation in NaOMe. At current densities $\geq 100 \text{ mA cm}^{-2}$, a more formaldehyde is produced at higher flow rates. At the lower flow rate, more formic acid is produced across all current densities. A similar behavior is observed for NaClO_4 , however, the trend is less pronounced compared to NaOMe.

In conclusion, the Faraday efficiency does not change with the NaOMe concentration across different flow rates at 3 mA cm^{-2} . At 100 mA cm^{-2} , however, there is a significant influence of the electrolyte concentration as well as the flow rate. The effects of the electrolyte concentration was first observed in the H-cell with decreasing Faraday efficiency at high NaOMe concentrations and at elevated current densities ($\geq 80 \text{ mA cm}^{-2}$, see also section 6.2).

Overall, a lower NaOMe concentration as well as higher flow rates favor the formaldehyde formation. These results match the observations by Haisch *et al.* who reported a beneficial influence of a high mass transport for the formaldehyde formation in aqueous alkaline electrolytes.^[31] The effects of the electrolyte concentration on the formaldehyde formation are investigated in more detail in chapter 8.

7.5 Electrode gap

All previous flow cell experiments were carried out with 8 mm gasket layers that formed the electrolyte channels between the electrodes. The real electrode distance during the experiment was smaller as the gasket layers were compressed when the cell was tightened. A smaller electrolyte gap, while keeping a constant flow rate, increases the mass transport on the electrode surface, which is expected to favor the formaldehyde formation. To investigate these effects, two different gasket configurations of 4 mm and 12 mm thickness were studied in 0.1 mol L^{-1} and 1.0 mol L^{-1} NaOMe at 10 mA cm^{-2} and 100 mA cm^{-2} . The calculated Faraday efficiencies are shown in Figure 7.11.

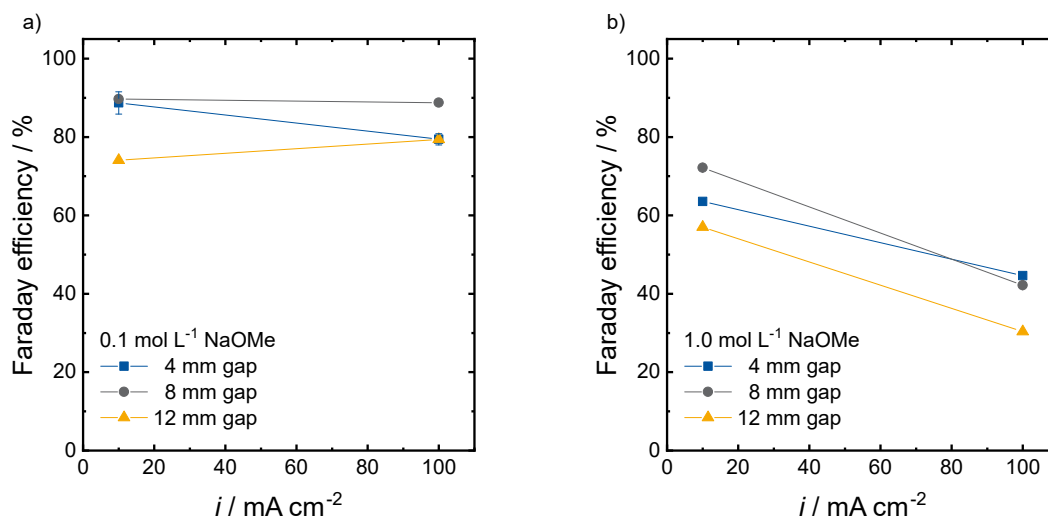


Figure 7.11: Faraday efficiencies for formaldehyde in a) 0.1 mol L⁻¹ and b) 1.0 mol L⁻¹ NaOMe on Pt at 10 mA cm⁻² and 100 mA cm⁻². The experiments were performed for 30 min with 40 mL electrolyte that was recirculated with 100 mL min⁻¹.

The Faraday efficiency for formaldehyde in 0.1 mol L⁻¹ NaOMe (Figure 7.11 a)) remains constant at 90 % for the 8 mm electrode gap at both current densities. The wider 12 mm electrode gap shows lower Faraday efficiencies compared to an 8 mm gap. But there is increase in the Faraday efficiency with increasing current densities from 74 % to 79 %. However, it remains unclear why the 12 mm electrode gap has a lower Faraday efficiency at 10 mA cm⁻². For the setup with an electrode gap of 4 mm, the opposite trend with a decrease in the Faraday efficiency from 89 % to 79 % with increasing current densities is observed. The data set shown in Figure 7.11 differs more than 5 % from the one shown in Figure 7.2 (78 %) at 10 mA cm⁻². Both data sets were measured by different experimenters and but only the newly measured data set is evaluated here to minimize the experimenter and material aging errors.

The same electrode gap variation was measured in 1.0 mol L⁻¹ NaOMe (Figure 7.11 b)). A decrease in the Faraday efficiency is observed for all electrode gaps. With a 4 mm gap, the Faraday efficiencies drops from 64 % to 45 % and a drop from 57 % to 30 % is observed for a 12 mm gap. The Faraday efficiency for the narrow gap drops by 19 percentage points (pp.) while it drops by 30 pp. for the 8 mm and by 27 pp. for the 12 mm distance. The Faraday efficiency for the 8 mm electrode gap at 10 mA cm⁻² shown in Figure 7.11 b) (72 %) also differs outside the measurement error from the one displayed in Figure 8.6 (62 %). Both data sets show a decrease of the Faraday efficiency with increasing current densities ending at 42 % and 44 %, respectively.

The different Faraday efficiency trends in 0.1 mol L^{-1} NaOMe may be caused by subsequent oxidation of formaldehyde. A short electrode distance increases the mass transport within the cell. This makes subsequent reactions of formaldehyde more likely when it comes in contact with either of the electrodes. In the 1.0 mol L^{-1} NaOMe electrolyte, the Faraday efficiency for all electrode gaps decreases with increasing current densities. Yet, it decreases the least for the 4 mm gap, and thus, a short electrode gap should be preferred for high NaOMe concentrations. This indicates that high mass transport caused by the short electrode gap outweighs the increased likelihood of formaldehyde oxidation.

The electrolyte gap does not only influence the reaction performance but also the cell voltage. At low current densities, the effects are minor but they become substantial at 100 mA cm^{-2} (Figure 7.12). A larger electrode gap means there is a larger electrolyte volume between the electrodes increasing the electrolyte resistance. To compare the effect of the electrode gap on the cell potential and the Faraday efficiency, the specific energy consumption E_s was calculated according to Equation 2.3 and are shown in Table A.12 for 0.1 mol L^{-1} and Table A.13 for 1.0 mol L^{-1} . The E_s decreases with smaller electrode gaps for both electrolytes indicating that the cell potential is the major influence. Thus, a smaller electrode gap should be preferred for a large scale synthesis.

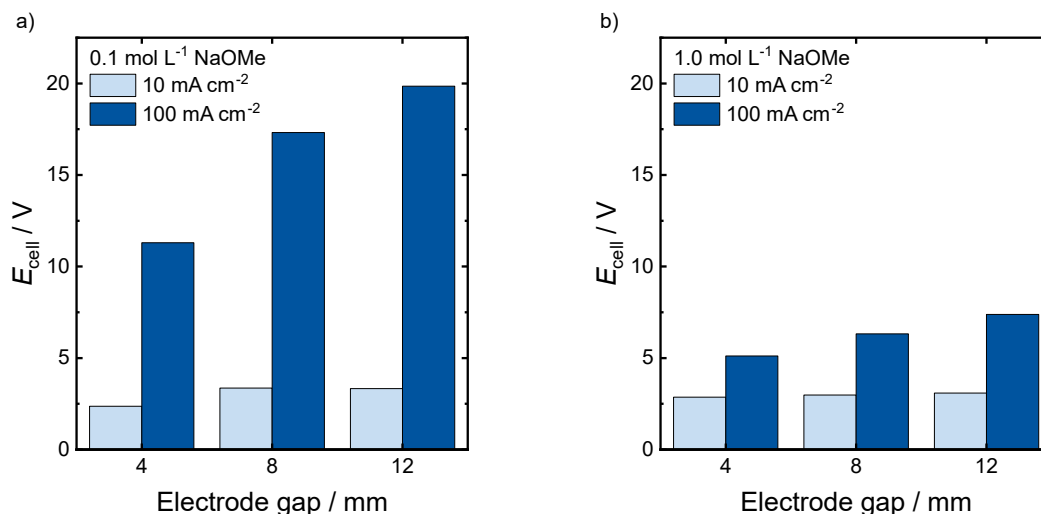


Figure 7.12: E_{cell} for the different electrode gaps at 10 mA cm^{-2} (light) and 100 mA cm^{-2} (dark) in a) 0.1 mol L^{-1} and b) 1.0 mol L^{-1} NaOMe.

7.6 Temperature

It was found that the 0.1 mol L^{-1} NaOMe electrolyte noticeably warmed during the variation of the current density (Figure 7.2). The temperature can influence the kinetics and thermodynamics of a reaction: an increased temperature enhances diffusion, increases the reaction rate and changes the required reaction potential.^[63] The electrolyte temperature for each current density was measured in the reservoir and is shown in Figure 7.13.

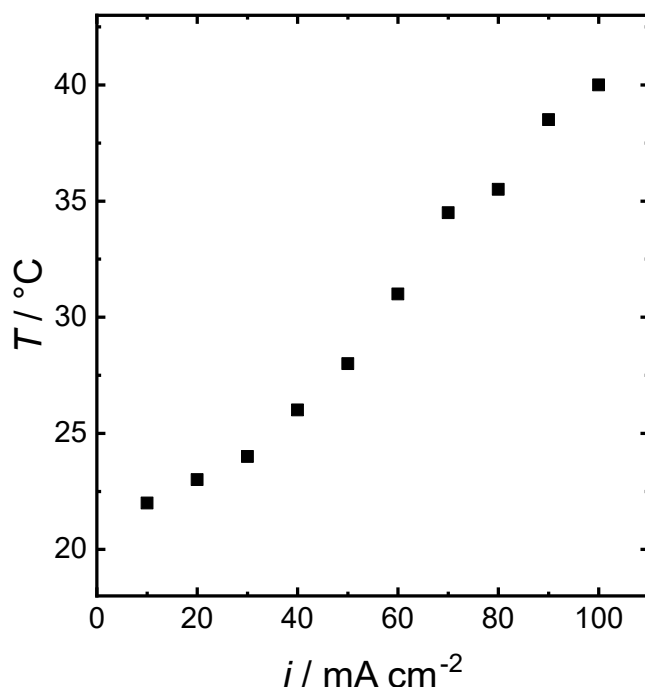


Figure 7.13: Temperature of the electrolyte reservoir after 30 min electrolysis in 0.1 mol L^{-1} NaOMe.

The temperature increases from 22°C at 10 mA cm^{-2} to 40°C at 100 mA cm^{-2} . The methanol dehydrogenation is an endothermic process, and thus, higher temperatures should favor the production of formaldehyde. Only a small temperature increase was observed for the 1.0 mol L^{-1} NaOMe electrolyte due to its higher conductivity, and hence, lower ohmic losses.

To investigate the temperature effect on the reaction selectivity, the 0.1 mol L^{-1} NaOMe electrolyte was once cooled with an ice bath to 10°C and in another experiment heated to 40°C . With these tempered electrolytes, CPs at varying current density were re-

peated. The Faraday efficiencies are shown in Figure 7.14. The Faraday efficiencies without temperature control starting at RT are shown in gray.

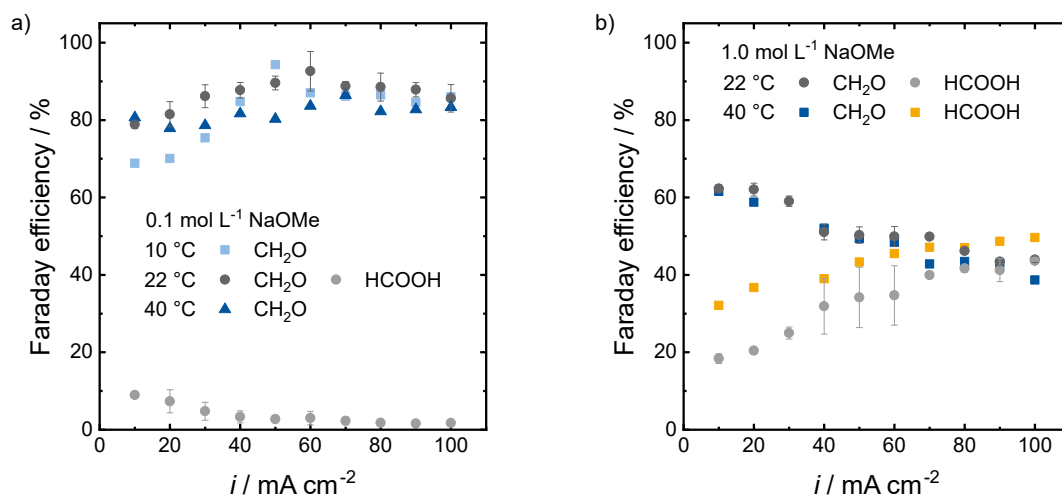


Figure 7.14: Faraday efficiencies for formaldehyde and formic acid at 10 °C, at RT and at 40 °C in a) 0.1 mol L⁻¹ NaOMe and b) 1.0 mol L⁻¹ NaOMe. The experiments were carried out on Pt with 40 mL electrolyte at a flow rate of 100 mL min⁻¹ for 30 min.

In 0.1 mol L⁻¹ NaOMe, cooling the electrolyte solution yielded lowered Faraday efficiencies for 10-30 mA cm⁻² (Figure 7.14 a)). At higher current densities, the Faraday efficiencies are comparable to the RT experiments. The trend for first increasing Faraday efficiencies between 10-60 mA cm⁻² and constant Faraday efficiencies afterwards remain similar for both 10 °C and RT. It is possible that the heat generated from the electrolyte resistance exceeds the cooling effect of the ice bath. The local temperature on the electrode might be even higher.

Heating of the electrolyte to 40 °C yielded comparable, but overall slightly lower Faraday efficiencies compared to the RT measurements. A difference in the Faraday efficiency is expected at low current densities during which the temperature difference should be the largest. It appears that heating the electrolyte to 40 °C does not significantly influence the formaldehyde formation. Yet, these Faraday efficiencies have to be confirmed as the measurement was only conducted once. More precise results can also be obtained by determining the temperature near the electrode surface or directly at the electrolyte outlet of the flow cell.

The temperature influence was also investigated for 1.0 mol L⁻¹ NaOMe. The electrolyte solution slightly warmed at high current densities. Only the heated electrolyte was tested as it was more likely to have a beneficial effect. The Faraday efficiencies for formaldehyde and formic acid are shown in Figure 7.14 b). The Faraday efficiencies

for formaldehyde are comparable for the RT and the heated electrolyte. It starts at 61 % at 10 mA cm^{-2} and decreases to 44 % at 100 mA cm^{-2} . The trend in the Faraday efficiency differs strongly from the one measured in 0.1 mol L^{-1} NaOMe, which is most likely caused by electrolyte effects. These are investigated and explained in more detail in chapter 8. Formic acid is produced in larger quantities, i.e., 20-44 % at RT and 32-50 % at 40°C . The increase in Faraday efficiency for formic acid averages 9 pp. with the largest difference of 16 pp. at 20 mA cm^{-2} . These differences in the formic acid formation might be caused by enhanced formic acid desorption from the electrode at higher temperature so it cannot oxidize further.

The temperature does not only influence the Faraday efficiency but also the electrolyte's conductivity and, thus, the cell potential (Figure 7.15).

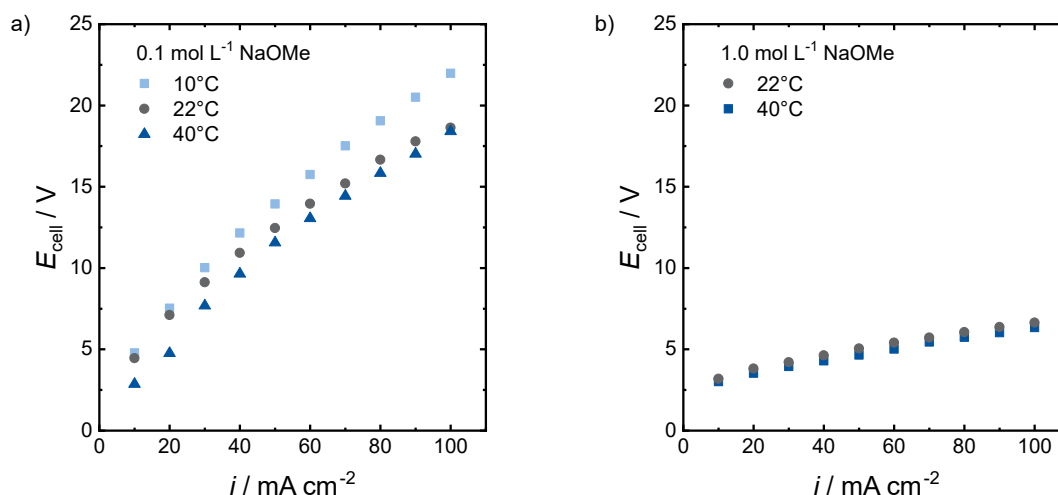


Figure 7.15: Cell potentials for formaldehyde in a) 0.1 mol L^{-1} and b) 1.0 mol L^{-1} NaOMe for different temperatures as a function of the current density. The experiments were performed on Pt for 30 min with 40 mL electrolyte that was recirculated with 100 mL min^{-1} .

For both electrolyte concentrations, the cell potential increases with the increasing current densities. For the 0.1 mol L^{-1} NaOMe electrolyte, the cooled electrolyte has the highest cell potentials. The cell potential for the RT series is close to the cooled one at low current densities, but it nears the heated electrolyte with increased current densities. The approach of the cell potentials of RT and 40°C at high current densities indicates that the lower cell potentials are caused by the increased reaction temperatures, which increases the electrolyte conductivity. The cell potential of the cooled electrolytes increases more strongly with increasing current densities up to a cell potential difference of 3.3 V at 100 mA cm^{-2} compared to the RT electrolyte.

These trends are not reflected in the Faraday efficiency. Despite the similar Fara-

day efficiencies of the cooled electrolyte and the RT one above 50 mA cm^{-2} , the cell potentials of the cooled electrolyte are significantly higher at current densities above 30 mA cm^{-2} . In 1.0 mol L^{-1} NaOMe, the cell potential is overall much lower ($\leq 6.6 \text{ V}$). The potential of the heated electrolyte is consistently $\leq 0.3 \text{ V}$ below the RT electrolyte. In both electrolyte concentrations, the heated electrolytes result in lower cell potentials but the difference is more pronounced in 0.1 mol L^{-1} NaOMe.

The electrolyte temperature influences the cell potential as well as the Faraday efficiencies. Heating the electrolyte lowers the required cell potential for both electrolyte concentrations, which is likely caused by the increased conductivity. An energy balance between heating and the reduced cell potential needs to be calculated to determine its economic feasibility.

Vastly different trends are observed for the temperature influence on the Faraday efficiencies to formaldehyde and formic acid. In the diluted electrolyte, cooling diminishes the Faraday efficiency at low current densities whereas the Faraday efficiencies remain constant for the heated electrolyte. At higher current densities, all three temperatures performed similarly. The detrimental effect of cooling shown in the cell potential was not mirrored in the Faraday efficiency. It might be possible that the endothermic reaction of the methanol oxidation to formaldehyde requires larger overpotentials to occur with the cooled electrolyte, which results in higher cell potentials.

In the 1.0 mol L^{-1} NaOMe electrolyte, the Faraday efficiency for formaldehyde remained unchanged upon heating the electrolyte to 40°C but the formic acid formation is enhanced. This indicates that formaldehyde is not converted to formic acid but instead subsequent reactions of formic acid are suppressed. Possible reasons may be the increased mass transport at higher temperatures that encourages formic acid desorption from the electrode surface. Alternatively, subsequent oxidation reactions, e.g., the total oxidation to CO_2 , may be exothermic and, thus, become less favored at higher temperatures. This is discussed in more detail in section 8.7. For a more detailed study of the temperature effects, the temperature has to be controlled more accurately and kinetic studies, e.g., Tafel analysis have to be conducted.

7.7 Overview of flow cell and scale-up effects

The transition and scale-up from the previously used H-cell to a flow cell setup changed a variety of setup and reaction parameters, such as flow rate, electrode gap and temperature, whose influence were investigated in this section. On the bases of previous small scale studies, different anode materials (Pt, Ni, Au) were tested with a larger surface area (12 cm^2) and at higher current densities (up to 100 mA cm^{-2}). Ni and Au were unstable at higher current densities because of metal dissolution. Pt remained stable and provided high Faraday efficiencies to formaldehyde. A smooth Pt surface leads to higher Faraday efficiencies than a rough one. Pt was also tested on carbon support, yet, the carbon support was not stable at higher current densities and it shifted the selectivity towards formic acid.

The variation of the flow rate shows that a high flow rate decreases the formation of formic acid, and thus a high flow rate is preferred. This also means that there is a shorter contact time for the molecules with the electrode surface indicating the formic acid formations occurs via a formaldehyde intermediate.

A similar effect is expected to be induced by varying the electrode gap. A small electrode gap lowers the Faraday efficiency in 0.1 mol L^{-1} NaOMe but performed comparably better in 1.0 mol L^{-1} NaOMe. Regardless of the electrolyte concentration, a smaller electrode gap always reduces the cell potential due to less ohmic losses caused by the electrolyte resistance.

Lastly, the temperature influence on the reaction was investigated. In 0.1 mol L^{-1} NaOMe, a high electrolyte temperature has a slight beneficial influence on the Faraday efficiency. In contrast, the Faraday efficiency for formaldehyde remains constant while the one for formic acid increases in 1.0 mol L^{-1} NaOMe. The cell potentials decrease at higher temperatures for both electrolyte concentrations.

Among the tested reaction and setup parameters, the following conditions are recommended for improved reaction performance: high flow rates for increased mass transport and a small electrode gap and a high temperature to reduce the energy requirements.

8 Influence of the supporting electrolyte

Previous experiments showed that the electrolyte composition has an immense effect on the selectivity of the anhydrous methanol oxidation. Thus, to investigate the electrolyte influence in more detail, a variety of supporting electrolytes were analyzed for their Faraday efficiency to formaldehyde. Among those, NaOMe, NaClO₄, LiOMe, and LiClO₄ were the most promising and were tested in-depth with respect to their physical and chemical properties and the influence on the formaldehyde formation. The solvent for the electrolyte was methanol in all experiments.

8.1 Electrolyte screening

The supporting electrolytes can be sorted into four different types: methoxide-based electrolytes (NaOtBu, LiOMe, NaOMe); perchlorate electrolytes (LiClO₄, NaClO₄, KClO₄); acidic (H₂SO₄); and alkaline (KOH). Please note that NaOtBu is considered as a methoxide electrolyte because it is more basic than methanol and can form *tert*-butanol and NaOMe by methanol deprotonation.^[185] The Faraday efficiency for formaldehyde in all electrolytes that provided a stable cell potential is shown in Figure 8.1. Two electrolyte concentrations, 0.1 mol L⁻¹ and 1.0 mol L⁻¹, in methanol were tested. Additional supporting electrolytes (CH₃COOH, H₃PO₄, KH₂PO₄, K₂HPO₄, Na₂SO₄) were tested, but were not further investigated because of their low conductivity or low solubility in methanol.

At low electrolyte concentrations (0.1 mol L⁻¹), all methoxide and perchlorate electrolytes as well as KOH show high Faraday efficiencies to formaldehyde (67 % (LiClO₄) to 83 % (NaOtBu)) with similar cell potentials between 3.9 V (NaOMe) and 4.8 V (NaClO₄). The cell potential of KClO₄ is 12.2 V caused by its low solubility in

methanol. The experiments using KClO_4 were performed in a saturated methanolic salt solution, which was filtered prior to measurement ($c < 0.1 \text{ mol L}^{-1}$). For methoxide and perchlorate electrolytes, the Faraday efficiency increases with increasing cation radius ($\text{Li} < \text{Na} < \text{K}$). H_2SO_4 provides the lowest overall cell potential (3.2 V) but no formaldehyde was detected after 30 min. As the sulfuric acid (95 %) used to prepare the electrolyte solution contained water, it is possible that methanol was fully oxidized to CO_2 .^[33,98] The KOH electrolyte achieved a Faraday efficiency of 78 %, which is similar to the Faraday efficiency of NaOMe, at a slightly higher cell potential of 4.2 V.

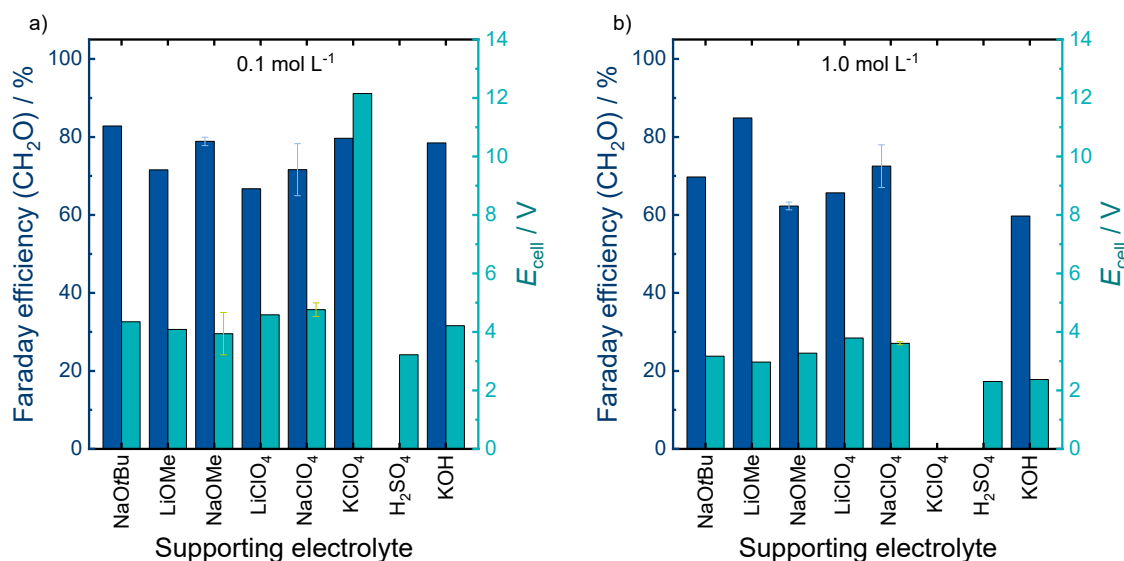


Figure 8.1: Faraday efficiency (blue) and the corresponding cell potentials (cyan) for different electrolytes with concentrations of a) 0.1 mol L^{-1} and b) 1.0 mol L^{-1} in methanol. The performance and potential were measured at an applied current density of 10 mA cm^{-2} .

With increasing electrolyte concentrations (Figure 8.1 b)), the Faraday efficiencies are lower (5-15 percent points (pps)), but also the cell potentials decrease significantly by approximately 25 % compared to the 0.1 mol L^{-1} electrolytes. The exception is LiOMe, which provides an increased Faraday efficiency of 85 %. Based on the single LiOMe measurement, which Faraday efficiency needs to be verified, the Faraday efficiency correlation with the cation size cannot be confirmed for the methoxide-containing electrolytes (62 % Faraday efficiency for NaOMe vs 85 % Faraday efficiency for LiOMe). For the perchlorate-containing electrolytes, the trend of increasing cation radii is also observed at concentrations of 1.0 mol L^{-1} . Higher electrolyte concentrations of the KClO_4 were not measurable due to its insufficient solubility in methanol. In methanolic KOH, formaldehyde is produced with a slightly lower Faraday efficiency but also a lower cell potential compared with the methoxide- and perchlorate-based electrolytes.

The beneficial effect of the increasing cation radius is consistent for methoxide and perchlorate electrolytes in 0.1 mol L^{-1} . While the same trend is observed for 1.0 mol L^{-1} perchlorates, it was not confirmed for the methoxide electrolytes. This indicates that not only the cation plays a role in the reaction performance but also the anion. Thus, the effects of the individual ions are investigated in more detail.

8.2 Electrolyte characterization

Out of the tested electrolytes, LiOMe, NaOMe, LiClO₄ and NaClO₄ were characterized in more detail, as they each differ in either cation or anion to two other salts (Figure 8.2). This allows to investigate the ion influence of the electrolytes and the electrolyte properties. The acid-base properties are known to be hugely influential on the occurring electrochemical reaction pathway.^[33,52] Furthermore, the viscosity and the conductivity of the electrolytes were measured as they are important process parameters for industrial application.

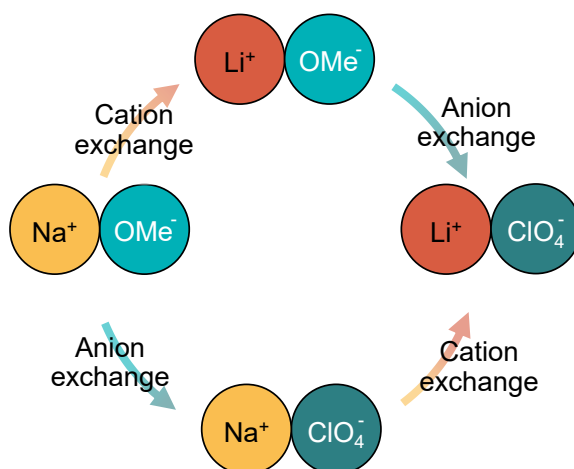


Figure 8.2: Overview of the ion exchange of the electrolyte variation.

8.2.1 Acid-base properties

The acid-base properties are often described by the pK_a value that represents the acid strength of a substance. The lower the pK_a value the stronger the acid. More details of the acid-base properties, especially in anhydrous electrolytes, are discussed in subsection 2.2.1. The investigated supporting electrolytes are salts of the corresponding

acids. Thus, the pK_a values for the acids were taken from literature with $pK_a = 15.5$ for HOMe and $pK_a = -1.6$ for HClO_4 .^[55] The pK_a scale is defined by an aqueous environment. Yet, pK_a values can also provide a good estimation of the acid-base properties in anhydrous methanol. HClO_4 is a very strong acid, and thus, its salts are very weak bases or can even be considered neutral. Methanol has a low acidity and the methoxide salts (X-OMe) are highly alkaline and would deprotonate water. The alkalinity of all methoxide salts used as electrolytes is, among others, dependent on the ion pairing in the methanolic solution and increases in the order $\text{Li} < \text{Na} < \text{K}$,^[186] which matches the hard and soft acids and bases (HSAB) theory.^[187] Potassium is a larger atom than, e.g., sodium, which means that is easier polarizable and requires less hydration energy.

8.2.2 Viscosity

The viscosity of the electrolyte influences the mass transport. A significant viscosity difference was visually observed for NaOMe electrolytes with increasing concentrations. Thus, the viscosity for all four electrolytes was measured as described in subsection 4.3.5, which allows a systematic analysis of the anion's and cation's influence. The measured viscosities are shown in Figure 8.3 at 0.1 mol L^{-1} (blue) and 1.0 mol L^{-1} (green), respectively. As expected, the viscosity of all supporting electrolytes at 0.1 mol L^{-1} is similar to methanol (dotted line). At 1.0 mol L^{-1} , the methoxide electrolytes are more viscous than the perchlorate ones whereas the lithium salts have a higher viscosity than the sodium salts. The viscosity measurements also show that the anion's influence on the viscosity is larger than the cation's influence for the tested electrolytes. These trends could be explained by taking electrostatic and intermolecular interactions into account. The Coulombic interactions of lithium-containing salts are stronger than for sodium-based salts due to a more concentrated charge distribution for the Li^+ cation. The Coulombic interactions within an electrolyte are also affected by its alkalinity and, thus, by the dissociation of the salt within the solvent. The latter is higher for the perchlorates compared to the methoxides. In addition, methoxide-based electrolytes can further attractively interact intermolecularly, clarifying the overall trend of viscosities: $\text{NaClO}_4 < \text{LiClO}_4 \ll \text{NaOMe} < \text{LiOMe}$.

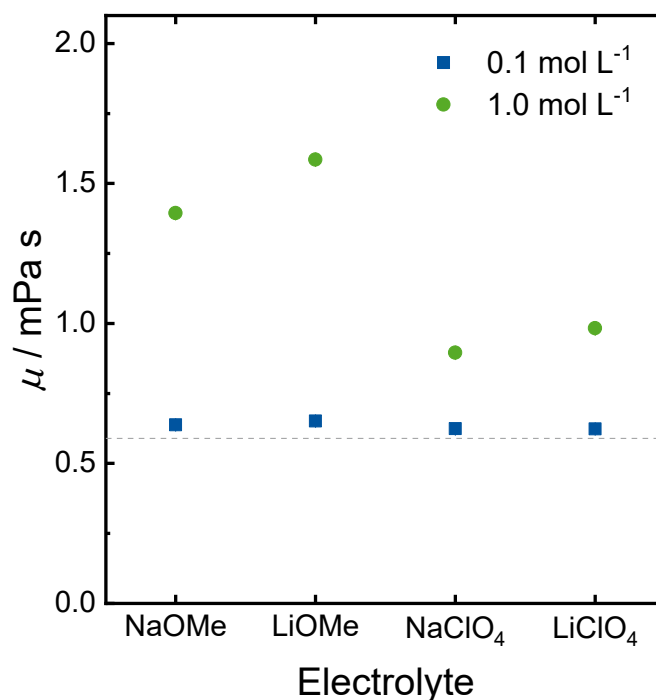


Figure 8.3: Viscosity of NaOMe, LiOMe, NaClO₄, LiClO₄ in concentration of 0.1 mol L⁻¹ (blue) and 1.0 mol L⁻¹ (green). The gray line indicates the viscosity of pure methanol. The error of determination for all data points is $\leq 4 \mu\text{Pa s}$.

8.2.3 Conductivity

Varying the supporting electrolyte also influences the ionic conductivity of the electrolyte. To compare the effects of the individual ions of the conducting salt, the conductivities of methanolic NaOMe, LiOMe, NaClO₄, and LiClO₄ were measured at 0.1 mol L⁻¹ and 1.0 mol L⁻¹ (Figure 8.4). For lower concentrated electrolytes ($c = 0.1 \text{ mol L}^{-1}$), the conductivities of the perchlorate salts (7.1 mS cm^{-1}) are only slightly higher compared to the methoxide salts (5.5 mS cm^{-1}) and independent of the cation. The conductivities for the 1.0 mol L⁻¹ electrolytes are, as expected, significantly higher than for the lower concentrations with perchlorate-based electrolytes (39.0 mS cm^{-1} for NaClO₄) being more conductive than methoxide-containing electrolytes (22.9 mS cm^{-1} for NaOMe). Remarkably, an influence of the electrolyte's cation is only observable for methoxide electrolytes (22.9 mS cm^{-1} for NaOMe vs. 16.7 mS cm^{-1} for LiOMe); for perchlorate salts, the cation has only a negligible influence.

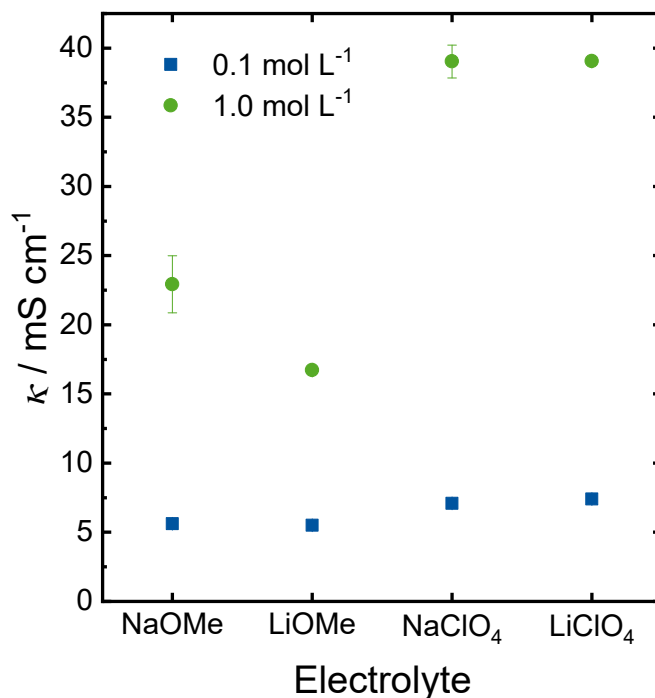


Figure 8.4: Conductivity of NaOMe, LiOMe, NaClO₄, LiClO₄ in concentration of 0.1 mol L⁻¹ (blue) and 1.0 mol L⁻¹ (green) at room temperature. Unless marked otherwise, the error of determination is $\pm 40 \mu\text{S cm}^{-1}$.

The conductivity of NaOMe and NaClO₄ was also measured across the concentration range 0.1–2 mol L⁻¹ (Figure A.10). The conductivity of NaOMe reaches a plateau of 21.4 mS cm⁻¹ at a concentration of 1.25 mol L⁻¹. At higher electrolyte concentrations, the conductivity drops. These conductivity curve matches the shape reported by Iwakura *et al.*, yet, their conductivities are three orders of magnitude higher.^[36] The conductivity of the perchlorate increases with increasing electrolyte concentrations from 7.1 mS cm⁻¹ at 0.1 mol L⁻¹ to 53.0 mS cm⁻¹ at 2.0 mol L⁻¹. A conductivity maximum was not measured but may be reached at higher perchlorate concentrations. In conclusion, the anion dominates the conductivity behavior. The higher conductivities of the perchlorate electrolytes indicate an increased ion mobility or degree of dissociation compared to the methoxide-containing electrolytes. This matches the results of the viscosity measurements. The perchlorate salts have a higher effective ion concentration due to the lower pK_a and a higher ion mobility due to fewer Coulombic and intermolecular interactions. For the methoxide-based electrolytes, there is a significant cation influence with stronger Coulombic interactions for the Li⁺ cation.

The cell potential at 100 mA cm^{-2} also changes significantly with the electrolyte concentration (Figure 8.5). Increasing the electrolyte concentration to 1.0 mol L^{-1} reduces the cell potential by 60 % for the methoxides and by 50 % for the perchlorates. The conductivity of the electrolytes also allows an iR correction of the measured cell potentials (Equation 8.1).

$$E_{\text{corr}} = E_{\text{cell}} - E_{iR} = E_{\text{cell}} - I \frac{d}{\kappa A} \quad (8.1)$$

For the correction, an electrode gap (d) of 8 mm was assumed as it is the thickness of the gasket layers. Any electrode gap reduction by tightening the cell is neglected. The corrected cell potentials for all electrolytes are between 1-3.8 V across all concentrations at 100 mA cm^{-2} (Figure 8.5).

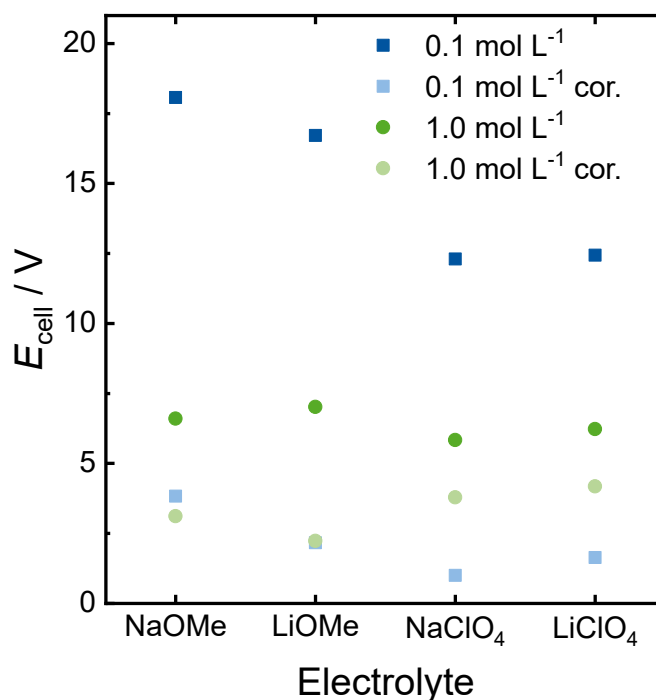


Figure 8.5: Cell potentials for different electrolytes at 100 mA cm^{-2} at 0.1 mol L^{-1} (blue) and 1.0 mol L^{-1} (green) without iR correction (dark colors) and with iR correction (light colors). The cell potentials were measured when a current density of 100 mA cm^{-2} flowed through the cell.

In 0.1 mol L^{-1} , the perchlorates have the lowest corrected potentials (E_{corr}) while they provide the highest E_{corr} in 1.0 mol L^{-1} . In contrast, E_{corr} for the methoxide electrolytes are independent of the electrolyte concentration. The different behaviors indicate that the electrolytes have different interactions with the reaction mechanism.

A perchlorate-based electrolyte facilitates the methanol oxidation to formaldehyde but high concentrations cause higher overpotentials. It is possible that a thicker ionic double layer forms on the electrodes that hinder the adsorption of methanol. For the methoxide electrolytes, E_{corr} is not affected by the concentration. A double layer on the anode consisting of OMe^- is still available for the methanol oxidation without introducing additional overpotentials.

Please note that this potential correction is an approximation that was made after the electrochemical measurement. For more accurate potential determination, the iR drop should be measured directly in the cell under flow conditions in a three electrode setup. These corrected potentials show that the reaction requires only a part of the energy and the majority is lost due to ohmic losses by poorly conducting electrolytes and a large electrode gap. Both, the electrolyte and the reactor design, can be optimized to enable industrial applicability of the methanol oxidation of anhydrous methanol.

8.3 Influence of the electrolyte on the electrochemical performance

The characterized electrolytes were also investigated in more detail for their performance for the electrochemical methanol oxidation to formaldehyde. Current densities between $10\text{--}100\text{ mA cm}^{-2}$ were step-wise applied and the Faraday efficiency was calculated. To discuss the influence of the alkalinity, KOH was also measured at 0.1 mol L^{-1} and 1.0 mol L^{-1} at only 10 mA cm^{-2} and 100 mA cm^{-2} .

8.3.1 Methoxide electrolytes

NaOMe had already been tested in the flow cell with 0.1 mol L^{-1} concentration (Figure 7.2, see chapter 7). 1.0 mol L^{-1} NaOMe was measured and described in detail as part of the temperature investigations (Figure 7.14, see section 7.6). The experiments were repeated and the previously detected trends were confirmed (Figure 8.6) In 0.1 mol L^{-1} , the Faraday efficiency initially increases and then stays constant between 80-90 % when the current density is increased. In 1.0 mol L^{-1} , however, the Faraday efficiency starts at 62 % and then decreases to 44 %. Formic acid is, instead, formed in larger quantities in 1.0 mol L^{-1} NaOMe.

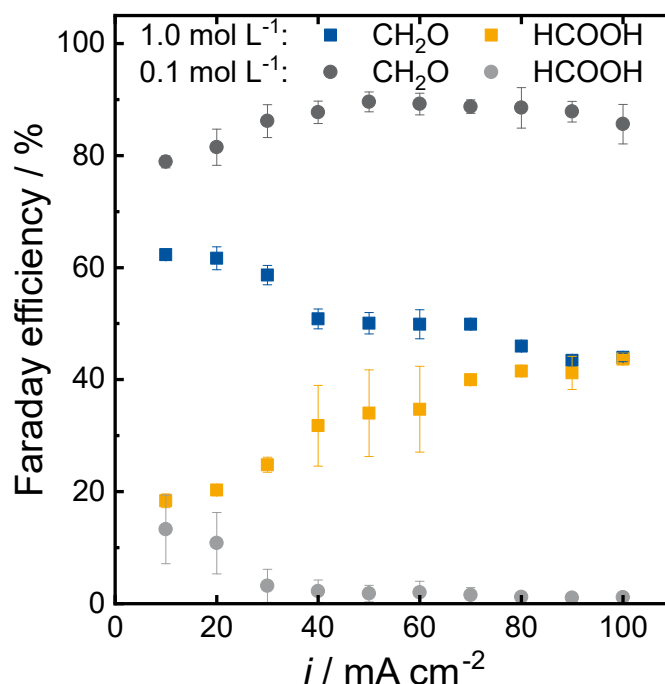


Figure 8.6: Faraday efficiencies for formaldehyde (blue) and formic acid (orange) 1.0 mol L^{-1} NaOMe as a function of the current density. The Faraday efficiency for the same products in 0.1 mol L^{-1} NaOMe are shown in gray. The reaction was performed on a Pt foil for 30 min with 40 mL electrolyte and a flow rate of 100 mL min^{-1} .

By exchanging the cation from Na to Li, the methoxide becomes less alkaline.^[186] At high concentrations, it is less conductive but more viscous. The Faraday efficiencies for formaldehyde and formic acid are shown in Figure 8.7 for 0.1 mol L^{-1} (a)) and 1.0 mol L^{-1} (b)). At low LiOMe concentrations, the Faraday efficiency for formaldehyde is constant between 70-80 % across all current densities. Formic acid was only detected at low current densities. At higher current densities, formic acid was not detected via HPLC due to an HPLC error. At 1.0 mol L^{-1} LiOMe, the Faraday efficiency for formaldehyde decreased with increasing current densities similar to the experiments carried out in NaOMe. In contrast, formic acid shows a slight increase with increasing current densities. The total Faraday efficiencies for all experiments surpass 100 %. There may be an overestimation of the Faraday efficiencies due to inaccuracies in HPLC measurement and interpretation. Overall, the trends obtained for LiOMe are similar to the ones for NaOMe. As all LiOMe experiments were only carried out once, all of the data points need to be verified.

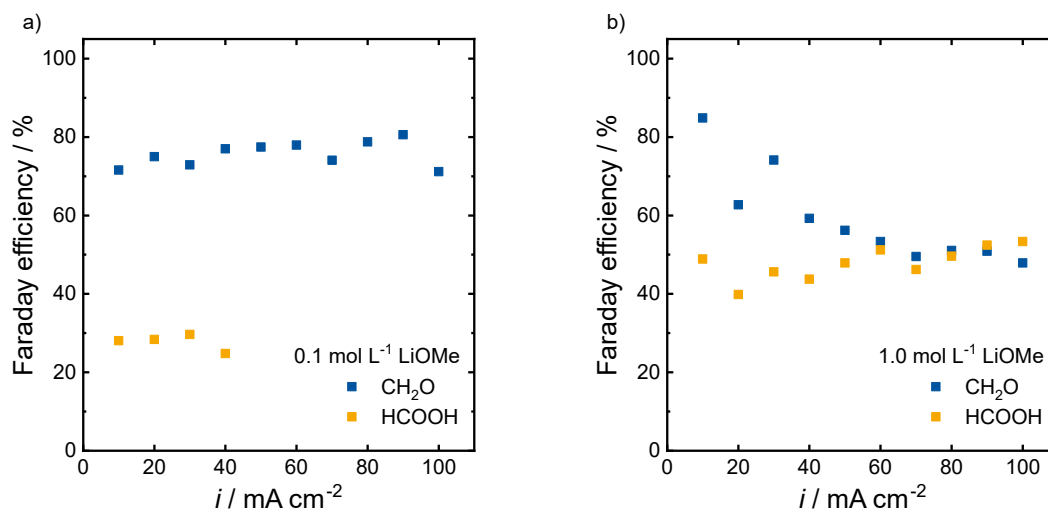


Figure 8.7: Faraday efficiency for formaldehyde (blue) and formic acid (orange) in a) 0.1 mol L⁻¹ and b) 1.0 mol L⁻¹ LiOMe as a function of the current density. The experiments were performed on Pt for 30 min with 40 mL electrolyte that was recirculated with 100 mL min⁻¹.

8.3.2 Perchlorate electrolytes

NaClO₄ and LiClO₄ were also investigated as supporting electrolytes in 0.1 mol L⁻¹ and 1.0 mol L⁻¹ in dependency of the applied current densities. The Faraday efficiencies for formaldehyde and formic acid of NaClO₄ are shown in Figure 8.8. At a concentration of 0.1 mol L⁻¹, NaClO₄ yielded constant Faraday efficiencies for formaldehyde between 70-80 % (Figure 8.8 a)). Formic acid is produced in larger amounts compared to NaOMe, but it shares the same trend of decreasing Faraday efficiencies with increasing current densities. The same behavior with even slightly higher Faraday efficiencies for formaldehyde was found for 1.0 mol L⁻¹ NaClO₄.

The Faraday efficiencies with 1.0 mol L⁻¹ NaClO₄ show a significantly different behavior compared to the methoxide electrolytes. The Faraday efficiency for formaldehyde was not only higher compared to the diluted electrolyte, but it was also stable across the different current densities. Formic acid was detected for 10 mA cm⁻² and 100 mA cm⁻², which were measured by one experimenter. The whole series was repeated twice by another experimenter and no formic acid was detected. The trend for the formic acid formation is analogous as in 0.1 mol L⁻¹ NaClO₄.

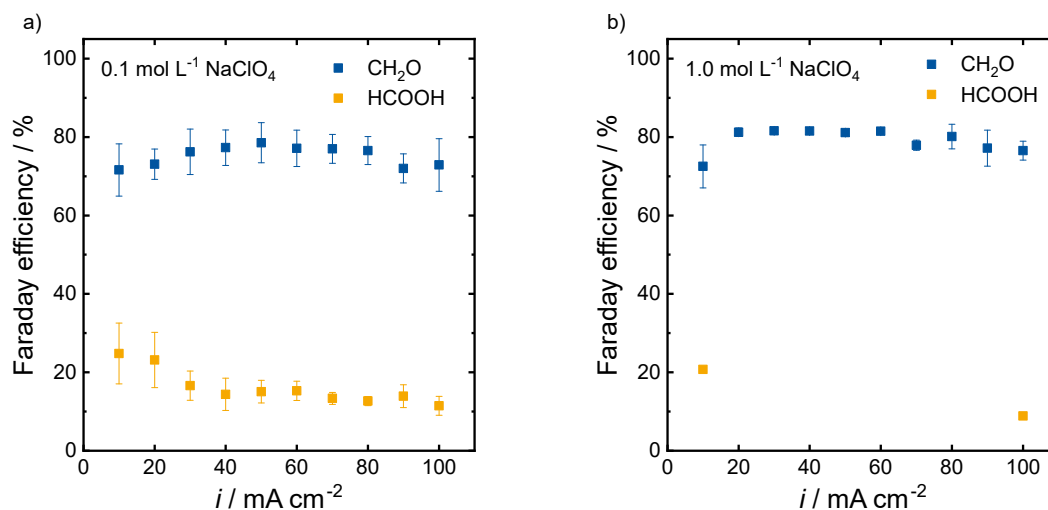


Figure 8.8: Faraday efficiency for formaldehyde (blue) and formic acid (orange) in a) 0.1 mol L⁻¹ and b) 1.0 mol L⁻¹ NaClO₄ as a function of the current density. The experiments were performed on Pt for 30 min with 40 mL electrolyte that was recirculated with 100 mL min⁻¹.

The Faraday efficiencies for 0.1 mol L⁻¹ and 1.0 mol L⁻¹ LiClO₄ are shown in Figure 8.9. Both LiClO₄ concentrations show a similar behavior. The Faraday efficiency for formaldehyde stays between 60-75%. In the higher concentrated electrolyte, the Faraday efficiency slightly decreases at higher current densities. Similar to NaClO₄, the concentration has little influence on the Faraday efficiency.

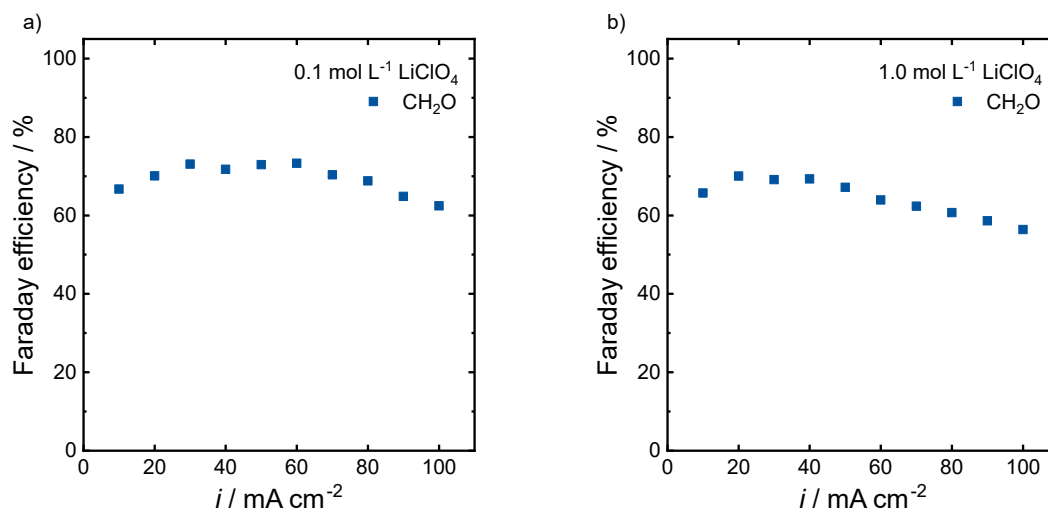


Figure 8.9: Faraday efficiencies for formaldehyde in a) 0.1 mol L⁻¹ and b) 1.0 mol L⁻¹ LiClO₄ as a function of the current density. The experiments were performed on Pt for 30 min with 40 mL electrolyte that was recirculated with 100 mL min⁻¹.

8.3.3 Potassium hydroxide

Potassium hydroxide (KOH) was additionally investigated to get a better understanding of the alkalinity influence. As initial experiments, KOH was tested in two concentrations (0.1 mol L^{-1} and 1.0 mol L^{-1}) at 10 mA cm^{-2} and 100 mA cm^{-2} . The Faraday efficiencies for formaldehyde and formic acid are shown in Figure 8.10.

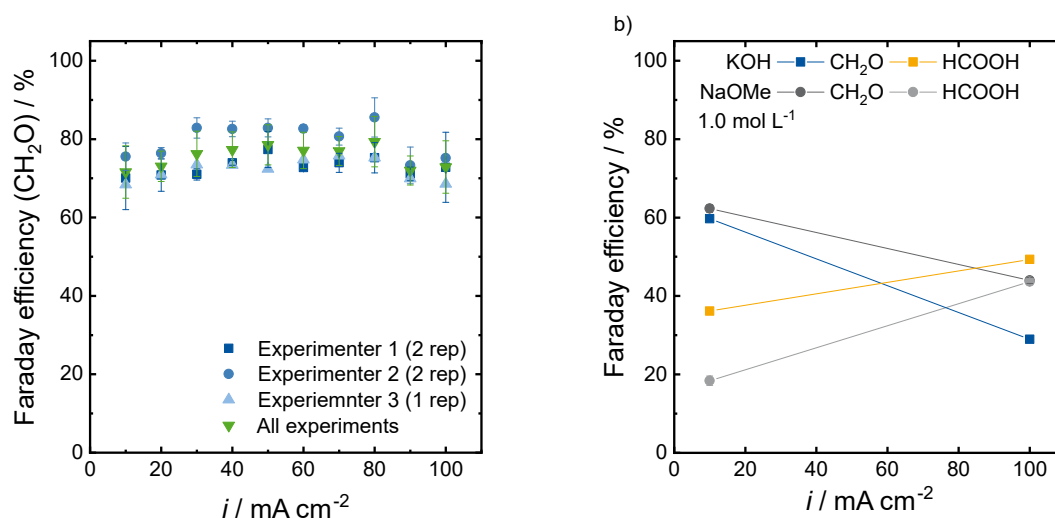


Figure 8.10: Faraday efficiency for formaldehyde (blue) and formic acid (orange) in a) 0.1 mol L^{-1} and b) 1.0 mol L^{-1} KOH as a function of the current density. The experiments were performed on Pt for 30 min with 40 mL electrolyte that was recirculated with 100 mL min^{-1} .

The experiments in 0.1 mol L^{-1} KOH result in similar Faraday efficiencies as the ones in NaOMe at the same concentration. Formaldehyde is produced in the same amount at both current densities (78%). Formic acid was not detected.

For the 1.0 mol L^{-1} electrolytes, similar trends can be observed for KOH and NaOMe, but they are more pronounced for KOH. The Faraday efficiency for formaldehyde drops more steeply while the formation of formic acid is comparable to NaOMe with increasing current densities. Overall, less formaldehyde and more formic acid are formed compared to NaOMe. KOH is a strongly alkaline supporting electrolyte. In accordance with previous found trends for the concentration of alkaline supporting electrolytes, these results indicate that a high alkalinity favors the formation of formic acid over formaldehyde.

8.3.4 Direct comparison of the different supporting electrolytes

The performance of the different supporting electrolytes (NaOMe, LiOMe, NaClO₄, LiClO₄) are evaluated by comparing the respective Faraday efficiencies for formaldehyde and the specific energy consumptions (E_s). Both evaluation parameters are analyzed with respect to the electrolyte properties. An overview of the Faraday efficiencies for the four electrolytes is shown in Figure 8.11. NaOMe was chosen as the reference electrolyte.

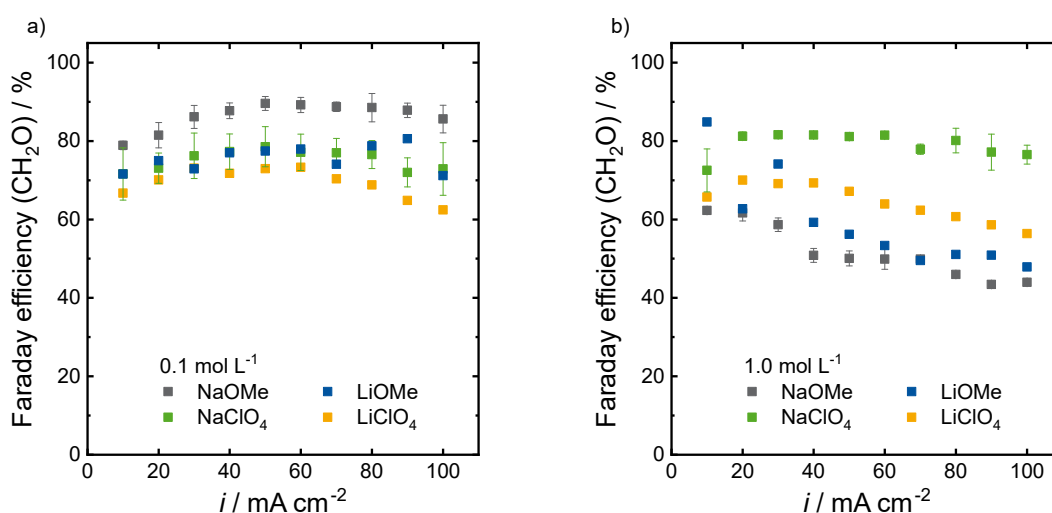


Figure 8.11: Comparison of the Faraday efficiency for formaldehyde in a) 0.1 mol L⁻¹ and b) 1.0 mol L⁻¹ in different electrolytes as a function of the current density. The experiments were performed on Pt for 30 min with 40 mL electrolyte that was recirculated with 100 mL min⁻¹. Error bars are shown for NaOMe and NaClO₄, the other data points are single determinations.

At 0.1 mol L⁻¹ (Figure 8.11 a)), all electrolytes perform slightly worse than the reference electrolyte NaOMe with Faraday efficiencies between 79-90 %. Nevertheless, in all electrolytes, stable Faraday efficiencies >60 % are obtained. The use of LiOMe and NaClO₄ results in similar Faraday efficiencies while using LiClO₄ produced the lowest Faraday efficiencies. In general, the methoxide electrolytes perform better than the perchlorate ones with higher Faraday efficiencies for the sodium salts. The reaction performance is, among others, dominated by the electrolytes' acid-base properties. Despite the low 0.1 mol L⁻¹ concentration and its rather low overall alkalinity, the experiments indicate that some alkalinity promotes the oxidation of methanol to formaldehyde and/or inhibits subsequent reactions. The viscosity for all electrolytes is similar to that of pure methanol and no influence can be expected.

The performance of the supporting electrolytes differs strongly when using 1.0 mol L^{-1} electrolytes (Figure 8.11 b)). Here, NaClO_4 yields the highest Faraday efficiencies and it is the only supporting electrolyte whose Faraday efficiencies increased at higher concentration. The obtained Faraday efficiencies for LiClO_4 remain rather constant whereas the ones for the methoxide salts decrease. LiClO_4 performs better than both methoxide salts while NaOMe results in the lowest Faraday efficiencies to formaldehyde.

For both methoxide and perchlorate electrolytes, the conductivity and viscosity increase with increasing concentration. However, the alkalinity is expected to remain near neutral for the perchlorates but to increase majorly for the methoxides. This suggests that too highly alkaline electrolytes might disfavor the formation of formaldehyde. Instead, formic acid is produced in increasing amounts, indicating that a different reaction pathway becomes preferred. Looking at the alkalinity of the individual salts, the use of LiOMe results in slightly higher Faraday efficiencies while being less alkaline than NaOMe ,^[186] This implies that the 1.0 mol L^{-1} methoxide electrolytes are too alkaline to favor formaldehyde formation. The opposite trend is observed with the perchlorate salts. Here, NaClO_4 performs better than LiClO_4 while being slightly more alkaline, according to the HSAB theory.^[187] This indicates that the perchlorates could benefit from adding alkalinity by, e.g., mixing supporting electrolytes. The viscosity of all electrolytes increases with increasing concentration, though less for the perchlorates. NaClO_4 yields the highest Faraday efficiencies while having the lowest viscosity indicating that a fast mass transport supports formaldehyde formation. For the methoxide electrolytes, NaOMe is less viscous than LiOMe but yields lower Faraday efficiencies. It is possible that the high viscosity of the 1.0 mol L^{-1} methoxide electrolytes reduces the mass transport near the electrode surface. The slowed mass transport increases the time that formaldehyde spends near the electrode, which leads to a subsequent formaldehyde oxidation to formic acid. Thus, it is possible that the high viscosity causes the shift in the product distribution from formaldehyde to formic acid. The investigated electrolyte properties cannot explain all the observed trends for the Faraday efficiencies, e.g., why, in 1.0 mol L^{-1} , NaClO_4 yields stable Faraday efficiencies but not LiClO_4 and why LiOMe performs better than NaOMe even though other experiments show better results for the sodium salts. Thus, additional factors of the electrolyte need to be taken into account.

While no correlation between the Faraday efficiency and the conductivity could be observed, it clearly influences the cell potential. The ratio between the required energy and the Faraday efficiency can be expressed via the specific energy consumptions E_s

(Equation 2.3, see section 2.1) In general, a high cell potential equals a high energy consumption while a high Faraday efficiency equals a low energy consumption. The E_s for all electrolytes is shown in Figure 8.12.

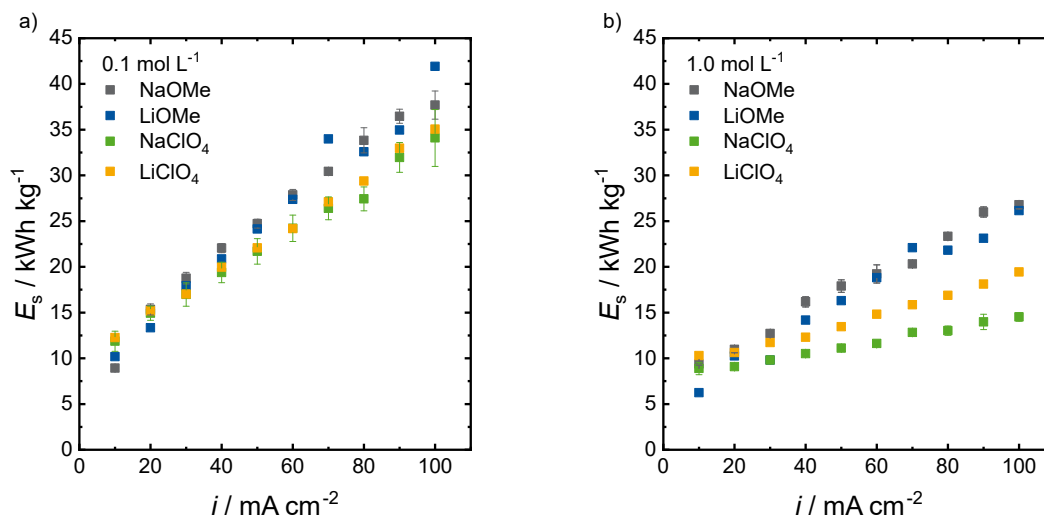


Figure 8.12: Comparison of E_s for formaldehyde in a) 0.1 mol L^{-1} and b) 1.0 mol L^{-1} in different electrolytes as a function of the current density. The experiments were performed on Pt for 30 min with 40 mL electrolyte that was recirculated with 100 mL min^{-1} . Error bars are shown for NaOMe and NaClO₄, the other data points are single determinations.

At a concentration of 0.1 mol L^{-1} , E_s for all electrolytes ranges between 9 kWh kg^{-1} (NaOMe) and 12 kWh kg^{-1} (LiClO₄) at 10 mA cm^{-2} and increases linearly with increasing current densities to a range of 34 kWh kg^{-1} (NaClO₄) to 42 kWh kg^{-1} (LiOMe). The Faraday efficiency is higher for the methoxide electrolytes than the perchlorate ones making the reaction overall more efficient. However, the E_s increases more steeply for the methoxide electrolytes. This steeper slope is likely caused by the conductivity difference of 2 mS cm^{-1} between the two electrolyte-types, which is comparatively large compared to the absolute values of 5 mS cm^{-1} for the methoxide and 7 mS cm^{-1} for the perchlorate electrolytes. This suggests that most of the energy is lost due to poorly conducting electrolytes and, thus, the major contribution to the E_s is the conductivity of the electrolytes.

The cell potentials of the Na-electrolytes are higher compared to the Li-electrolytes (Figure 8.13), while having a slightly lower viscosity and equal conductivity. As the Na-electrolytes also lead to higher Faraday efficiencies, it compensates for the higher cell potentials and the E_s for both methoxide- and perchlorate-salts overlap in 0.1 mol L^{-1} , regardless of the cation. Based on the electrolyte properties, a lower cell or at least equal cell potential for the Na-salts was expected as a lower viscosity should lead to

better mass transport. Yet, the cell potentials are higher for the Na-electrolytes, which indicates that the cation influences more than just the viscosity and the conductivity.

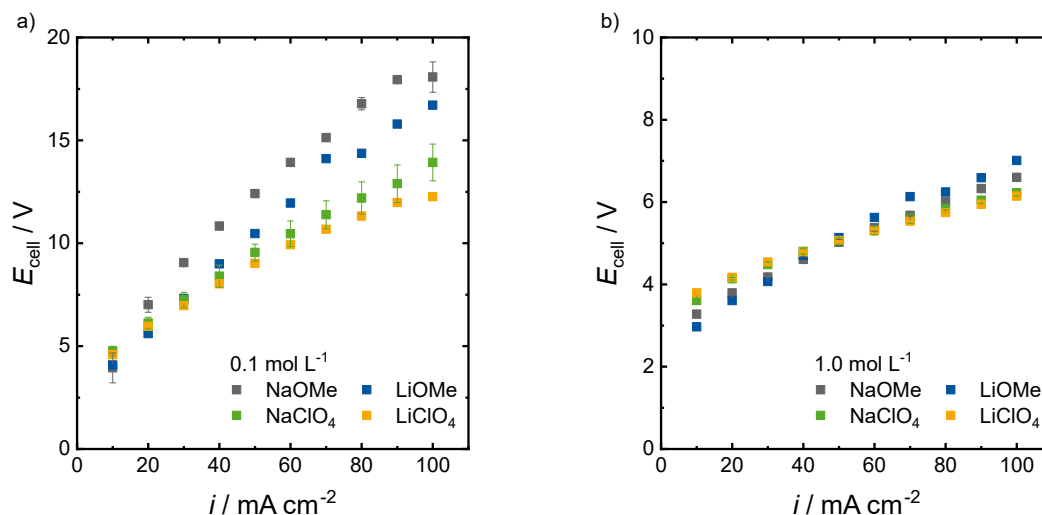


Figure 8.13: Cell potentials of the different electrolytes in a) 0.1 mol L^{-1} and b) 1.0 mol L^{-1} concentration as a function of the current density. The potential was averaged over 30 min. The experiment was run with 40 mL electrolyte that was recirculated with 100 mL min^{-1} . Error bars are shown for NaOMe and NaClO₄. In 1.0 mol L^{-1} , they are $\leq 90 \text{ mV}$ for both electrolytes.

For all 1.0 mol L^{-1} electrolytes, the E_s is in the range of 6 kWh kg^{-1} at 10 mA cm^{-2} (LiOMe) and 27 kWh kg^{-1} at 100 mA cm^{-2} (NaOMe, Figure 8.12 b)) and, thus, is lower compared to the diluted electrolytes. For the methoxide electrolytes, the E_s appears independent of the cation. Because of its lower conductivity, LiOMe has higher cell potentials (Figure 8.13) that are compensated by higher Faraday efficiencies. Both perchlorate salts have identical cell potentials, but the E_s for the NaClO₄ electrolyte is lower as higher Faraday efficiencies were achieved. The difference to LiClO₄ widens with increasing current densities as the Faraday efficiencies of formaldehyde decrease. The different slopes between the methoxide and perchlorate electrolytes are caused by the different conductivities. The cation choice of the electrolyte is less influential at higher electrolyte concentrations for the cell potentials and the E_s .

8.4 Electrolyte mixtures

Previous experiments showed that 0.1 mol L^{-1} NaOMe provides the highest Faraday efficiency for formaldehyde. However, its E_s was high due to the electrolyte's low conductivity. On the other side, 0.1 mol L^{-1} perchlorate supporting electrolytes have lower Faraday efficiencies but are more conductive. A mixture of both supporting electrolytes could possibly combine high selectivity and high conductivity. To investigate the performance of supporting electrolyte mixtures, different concentrations of NaClO₄ were added to a methanolic 0.1 mol L^{-1} NaOMe solution, and the Faraday efficiency was determined at 10 mA cm^{-2} and 100 mA cm^{-2} . The obtained Faraday efficiencies for formaldehyde and the corresponding specific energy consumptions are shown in Figure 8.14.

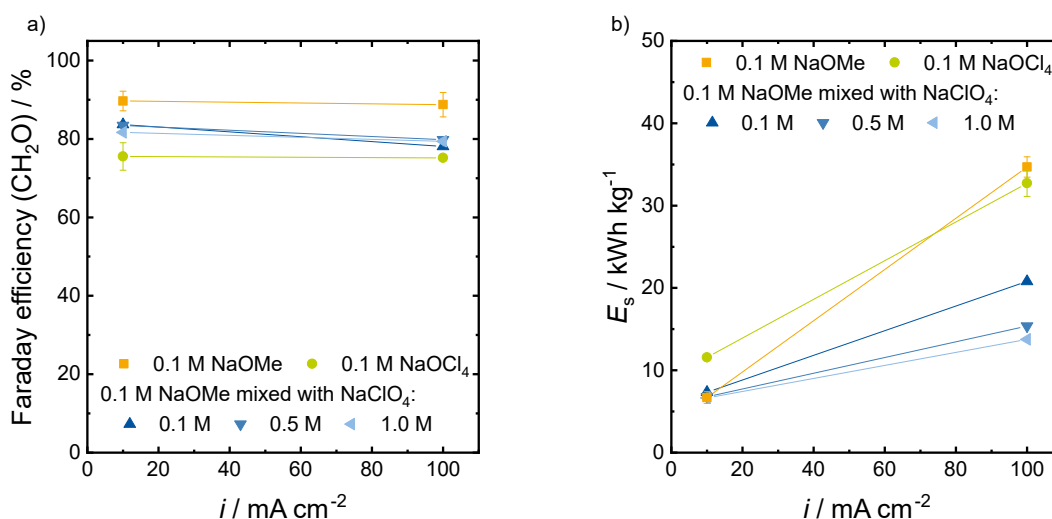


Figure 8.14: a) Faraday efficiency and b) E_s for 0.1 mol L^{-1} NaOMe with the addition of 0.1 , 0.5 and 1.0 mol L^{-1} NaClO₄. Pure 0.1 mol L^{-1} NaOMe (orange) and NaClO₄ (green) are shown for reference. The experiments were performed on a Pt WE for 30 min with 40 mL electrolyte that was recirculated with 100 mL min^{-1} .

The Faraday efficiencies of the mixed electrolytes are between the ones of the pure electrolytes. They show a downward trend with increasing current densities to approach the Faraday efficiency of pure NaClO₄ at 100 mA cm^{-2} . The addition of NaClO₄ decreases the Faraday efficiency by 5–10 pp. but the amount of added NaClO₄ does not have a remarkable influence on the Faraday efficiency decrease. However, mixing both supporting electrolytes lowers the specific energy consumptions significantly compared to the pure supporting electrolytes due to the higher conductivity of NaClO₄. The

addition of 1.0 mol L^{-1} NaClO_4 reduces the E_s by 60 % compared to pure 0.1 mol L^{-1} NaOMe (Figure 8.14 b). The mixed electrolytes also perform slightly better than pure 1.0 mol L^{-1} NaClO_4 with a higher Faraday efficiency by 6 pp. and a lower E_s by 0.8 kWh kg^{-1} . Thus, mixing electrolytes is a promising possibility to explore new reaction conditions for an industrial process to tailor the trade-off between the highest possible Faraday efficiency and a low overall E_s .

The influence of NaClO_4 addition was also investigated for 1.0 mol L^{-1} NaOMe at $10\text{--}100 \text{ mA cm}^{-2}$ (Figure 8.15).

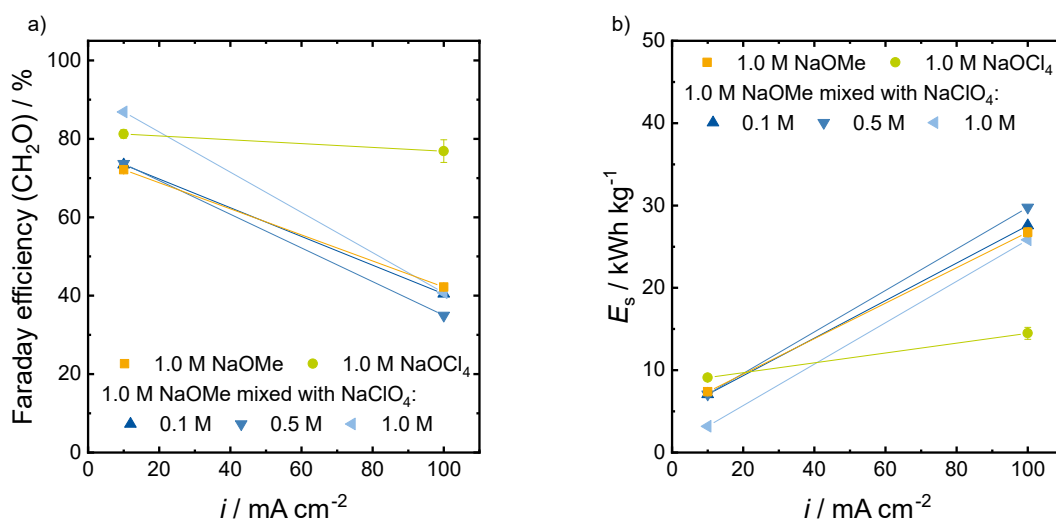


Figure 8.15: a) Faraday efficiency and b) E_s for 1.0 mol L^{-1} NaOMe with the addition of 0.1 , 0.5 and 1.0 mol L^{-1} NaClO_4 . Pure 1.0 mol L^{-1} NaOMe (orange) and NaClO_4 (green) are shown for reference. The experiments were performed on a Pt WE for 30 min with 40 mL electrolyte that was recirculated with 100 mL min^{-1} .

Here, the Faraday efficiency as well as the E_s are dominated by the 1.0 mol L^{-1} NaOMe . All Faraday efficiencies for the electrolyte mixtures show a downward trend with increasing current densities. At 10 mA cm^{-2} , pure NaOMe and the mixtures with 0.5 mol L^{-1} and 1.0 mol L^{-1} NaClO_4 have a Faraday efficiency of 73 %. The addition of 1.0 mol L^{-1} NaClO_4 increases the Faraday efficiency to 87 %. At 100 mA cm^{-2} , pure NaOMe , and mixtures with 0.1 mol L^{-1} and 1.0 mol L^{-1} NaClO_4 have a Faraday efficiency of 41 % but the addition of 0.5 mol L^{-1} NaClO_4 lowers it to 35 %. Please note that these are single determination experiments and they should be repeated to confirm the observed trends.

The E_s reflect the trends shown for the Faraday efficiencies with 1.0 mol L^{-1} NaClO_4 having the lowest E_s at 10 mA cm^{-2} and 0.5 mol L^{-1} NaClO_4 having the highest at 100 mA cm^{-2} . The E_s are all in the range of pure 1.0 mol L^{-1} NaOMe as the cell po-

tentials do not change with the addition of NaClO_4 . It is likely that the addition of NaClO_4 increases the conductivity of the electrolyte mixture. However, this is not reflected in a lower cell potential or E_s , respectively. This indicates that either the conductivity of the electrolyte mixture does, in fact, no increase or that the conductivity is not limiting factor for the cell potential above a certain threshold. It is also possible that the perchlorate introduces additional overpotentials if the perchlorate anions coordinate to the electrode, which limits the available adsorption site for methanol. The NaClO_4 addition has different effects on the E_s depending on the NaOMe concentration. The addition of NaClO_4 was beneficial for 0.1 mol L^{-1} NaOMe due to constant Faraday efficiencies but lower E_s . However, for 1.0 mol L^{-1} NaOMe, the Faraday efficiency and E_s remain unchanged. Further studies are required to understand the differences in behavior.

8.5 Influence of the alkalinity on the formic acid formation

The alkalinity can influence the electrochemical reaction but also enable or hinder subsequent chemical reactions. Thus, it was investigated whether formic acid forms due to an electrochemical reaction or due to the Cannizzaro reaction, which is a purely chemical one. The Cannizzaro reaction is the base-catalyzed disproportionation of two non-enolizable aldehydes to a primary alcohol and a carboxylic acid.^[188] In this case, formaldehyde can disproportionate to methanol and formic acid (Equation 8.2).



To investigate whether formic acid is formed via the Cannizzaro reaction, the NaOMe concentration was increased from 0.1 mol L^{-1} to 1.0 mol L^{-1} after the electrochemical experiment (100 mA cm^{-2} , 30 min, 40 mL). Three samples of the product solution were taken: 1) was not altered as a point of reference, 2) NaOMe concentration was increased by the addition of solid NaOMe (98 %), 3) NaOMe concentration was increased by 30 wt.% NaOMe in methanol, which slightly increased the sample volume. Option 3 used the same concentrated NaOMe solution that was used to prepare the electrolyte solution. Option 2 used solid NaOMe to alter the concentration without altering the sample volume. The solutions were then stored in the fridge for 72 h as it was the average time the samples were stored before the HPLC measurement. This procedure

was repeated with two different samples and the obtained formaldehyde and formic acid concentrations are shown in Table 8.1. If the Cannizzaro reaction occurs, higher formic acid concentrations are expected due to the increase of the base concentration.

Table 8.1: Amounts of formaldehyde and formic acid prior (1) and after the addition of NaOMe. 100 mA cm^{-2} were applied on a Pt WE to 40 mL of 0.1 mol L^{-1} NaOMe for 30 min. The NaOMe concentration was increased to 1.0 mol L^{-1} via solid NaOMe (2) and dissolved NaOMe in methanol (3).

n_{init} (CH_2O) mmol	n_{init} (HCOOH) mmol	increased with	n_{fin} (CH_2O) mmol	n_{fin} (HCOOH) mmol
2.3 (1)	0	98 % NaOMe (2)	1.9	1.5
2.3 (1)	0	30 wt.% NaOMe (3)	2.0	0
2.4 (1)	0	98 % NaOMe (2)	2.2	1.5
2.4 (1)	0	30 wt.% NaOMe (3)	2.4	0

Increasing the NaOMe concentration with solid NaOMe leads to a decrease in the formaldehyde concentration for both data sets. They also show an increase of the formic acid concentration by 1.5 mmol. According to the Cannizzaro reaction, two aldehydes disproportionate to one alcohol and one carboxylic acid.^[188] Thus, 0.4 mmol formaldehyde can react to 0.2 mmol formic acid. This theoretical amount is one order of magnitude lower than the detected amount of formic acid. As the formic acid change is substantially larger than the formaldehyde change, it is likely that formic acid is an impurity in the solid NaOMe, which has to be verified independently.

The use of dissolved NaOMe to increase the supporting electrolyte concentration gives ambiguous results. In the first data set, a slight decrease of the formaldehyde concentration is observed while it remains constant for the second data set. No formic acid was detected in both cases. The NaOMe solution was used to prepare all NaOMe experiments, so no formic acid impurity was introduced to the electrolytes. Therefore, the detected formic acid in higher supporting electrolyte concentrations must originate from an electrochemical reaction rather than a chemical formation via the Cannizzaro reaction.

8.6 Influence of the formaldehyde concentration

Formaldehyde is just one of the several possible oxidation products of the methanol oxidation reaction. It can potentially be oxidized further in case of repeated contact

with the anode. It is also possible for formaldehyde to be reduced whenever it reaches the cathode and hydrogen is present.

All flow cell experiments described in previous chapters were carried out with a recirculating electrolyte. Formaldehyde that had been produced in the first pass through the cell had a chance of reaction on the anode or cathode whenever it reenters the electrochemical cell. The chance increases with the number of passes and the formaldehyde concentration. The formaldehyde concentration in the solution is a function of the electrolyte volume, the current density and the reaction time. Time and current density provide the charge flowing through the electrochemical cell. The Faraday efficiency describes the amount of charge that actually goes into the formaldehyde formation. It is difficult to artificially increase the formaldehyde concentration as formaldehyde is either sold in aqueous solutions or as paraformaldehyde. The aqueous formaldehyde solution would introduce water to the reaction system, which enables more side reactions. Paraformaldehyde can be transformed to monomeric gaseous formaldehyde by heating.^[11] Because of the toxicity of formaldehyde, a gas tight setup would be needed where an amount of paraformaldehyde can be evaporated and the formaldehyde gas is dissolved in the electrolyte solution.

To investigate the influence of higher formaldehyde concentrations on the Faraday efficiency of the methanol oxidation, repeated single pass experiments were conducted. Each individual experiment was a single pass experiment, but the electrolyte was collected after each and then reused for the next pass. To limit material investment of the passes, the flow rate was set to 10 mL min^{-1} with 400 mL methanolic NaOMe electrolyte. A current density of 10 mA cm^{-2} was applied for 4 passes. After each pass, the electrolyte volume was refilled to 400 mL volume with methanol. No clear correlation between the number of passes and the Faraday efficiency was found for both 0.1 mol L^{-1} and 1.0 mol L^{-1} (Figure A.11). The experiment was repeated with a current density of 100 mA cm^{-2} for 8 passes, which equals a total of 4 h reaction time. Afterwards, the experiment was switched to electrolyte recirculation for a total experiment duration of 15 h and 20 h, respectively. The Faraday efficiency in 0.1 mol L^{-1} NaOMe is constant at around $73 \pm 4 \%$ for the first 4 h/8 passes (Figure 8.16 a)). The long term measurement for 0.1 mol L^{-1} NaOMe were interrupted after 10 h and 12 h due to the compliance voltage becoming too large (Figure A.12). The reason for this remains unclear, though, the restart of the experiment was possible with the remaining electrolyte solution. It might be possible that the ohmic resistance of the electrolyte heated it until it started to evaporate. The two interrupted measurements average to a total reaction time of 15 h with a Faraday efficiency of $54 \pm 2 \%$, which equals

6.3 ± 0.9 g formaldehyde produced. After 4 h, 2 ± 0.1 g formaldehyde were produced. With constant Faraday efficiencies, 7.3 g formaldehyde would have been expected but the obtained result is significantly lower. This indicates that an increasing formaldehyde concentration lowers the Faraday efficiency of the overall reaction.

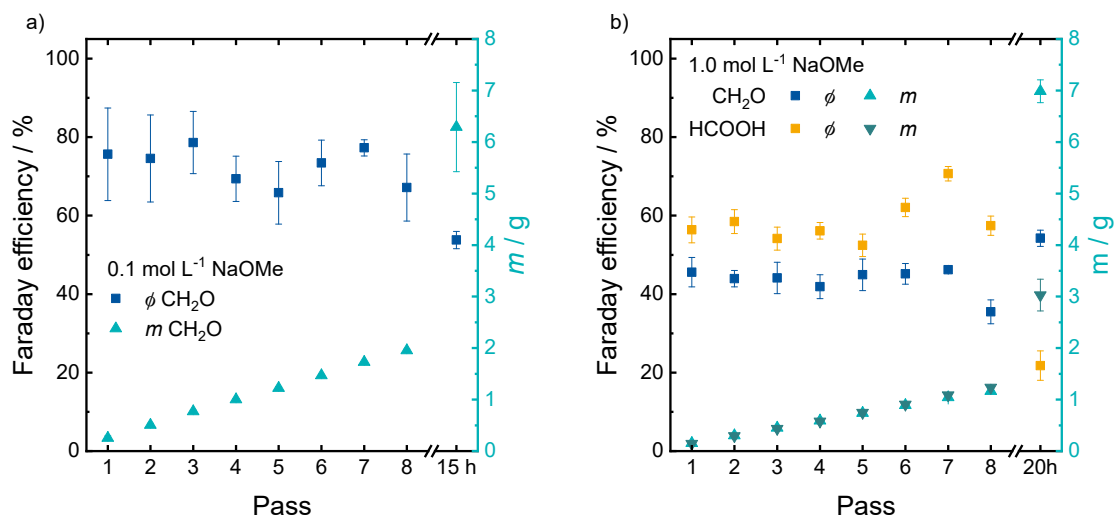


Figure 8.16: Faraday efficiency and product masses over 4 h and after 20 h for a) 0.1 mol L⁻¹ and b) 1.0 mol L⁻¹ NaOMe with a flow rate of 10 mL min⁻¹. Each pass was performed on Pt for 30 min with a current density of 100 mA cm⁻² with 400 mL electrolyte as a single pass with a flow rate of 10 mL min⁻¹. The electrolyte was then used for the subsequent pass.

In 1.0 mol L⁻¹ NaOMe, the Faraday efficiency for both formaldehyde and formic acid is constant around $45 \pm 1\%$ for 3.5 h after which it drops to $35 \pm 3\%$. During the first 4 h, the reaction is more selective for formic acid with an average of $58 \pm 5\%$, which peaks at 71% after 3.5 h. Afterwards, the selectivity to formic acid decreases and reaches an accumulated Faraday efficiency of 22% after 20 h. This indicates that the formic acid formation slows down drastically over time but it is still unclear what causes this slowing down. In contrast to the more diluted NaOMe electrolyte, the Faraday efficiency for formaldehyde does not drop after 20 h. Instead, it increases to $54 \pm 2\%$, which is now identical for both electrolyte concentrations. The Faraday efficiency for formic acid decreases to $22 \pm 3\%$. The decrease in the formic acid formation could indicate that a OH⁻ providing substance is consumed or that the viscosity of the electrolyte decreases. The lower viscosity allows faster formaldehyde removal from the electrode to avoid subsequent oxidation. The cause of the enhanced formaldehyde and the less efficient formic acid formations needs to be investigated further. After a total reaction time of 20 h, 7.0 g formaldehyde and 3.0 g formic acid were produced. Because of the longer reaction time, a higher formaldehyde concentration (17.5 g L⁻¹)

was achieved compared to the 0.1 mol L^{-1} NaOMe electrolyte (15.8 g L^{-1}). Regardless of the initial electrolyte concentration, both achieve identical Faraday efficiencies once they reach similar formaldehyde concentrations. This suggests that formaldehyde can subsequently react, and thus lower the overall Faraday efficiency at high conversion.

In a previous study (section 7.4), it was shown that a flow rate of 10 mL min^{-1} reduces the Faraday efficiency for formaldehyde. Thus, the experiment was repeated with $2000 \text{ mL } 0.1 \text{ mol L}^{-1}$ NaOMe and a flow rate of 100 mL min^{-1} with 15 min passes. The Faraday efficiencies for each pass and the additional 16 h recirculation is shown in Figure 8.17.

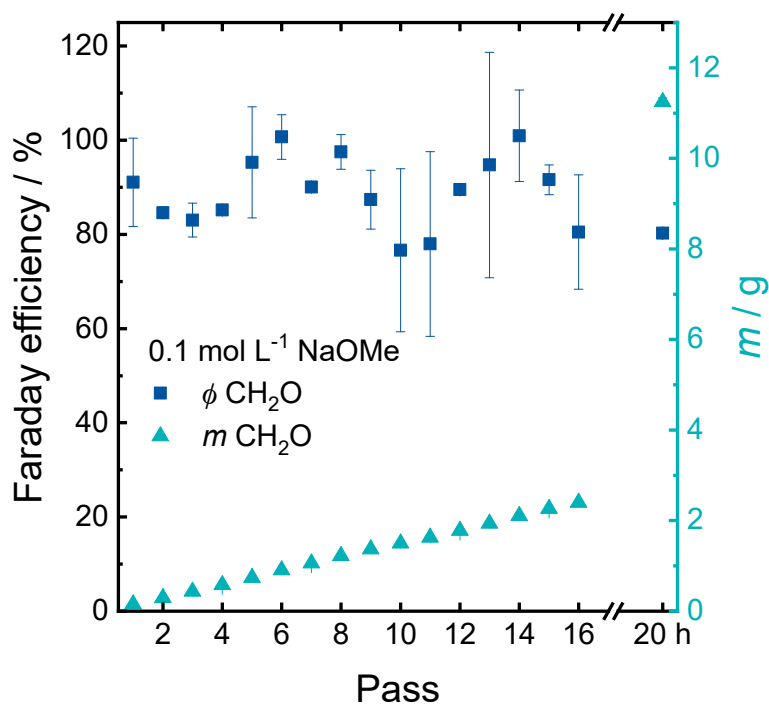


Figure 8.17: Faraday efficiency and product masses over 4 h and after 20 h for 0.1 mol L^{-1} NaOMe with a flow rate of 100 mL min^{-1} . Each pass was performed on Pt for 15 min with 2000 mL electrolyte as a single pass at 100 mA cm^{-2} . The electrolyte was then used for the subsequent pass.

For the first 4 h/16 passes, the Faraday efficiency for formaldehyde averages $90 \pm 8 \%$. This was expected as flow rates $\geq 50 \text{ mL min}^{-1}$ have been shown before to be beneficial for the selectivity towards formaldehyde. The larger error bars are caused by the difficulty in accurately collecting and measuring the total electrolyte volume after the experiment. After 20 h, the overall Faraday efficiency was 80% and 11.2 g formaldehyde

were detected, which equals a concentration of 5.6 g L^{-1} . Overall, the higher flow rate leads to higher Faraday efficiencies and an increased amount of formaldehyde after 20 h. Because of the larger reaction volume at the higher flow rate, the final formaldehyde concentration was lower by $\sim 2/3$ compared to the lower flow rate experiments. Thus, it cannot be confirmed that the high product concentration causes the lowered Faraday efficiency or whether the diminishing Faraday efficiency can be offset by a better mass transport. This can be differentiated by repeating the experiment with a longer reaction time until formaldehyde concentrations similar to the ones in the low-flow-rate study are reached.

It also remains unclear why the Faraday efficiency for formaldehyde drops due to formaldehyde oxidation or reduction. Introducing a separator to the flow cell can separate anolyte and catholyte. Formaldehyde is only formed on the anode so the formaldehyde reduction should be avoided. A separator would also allow the use of different electrolytes for each electrode. Its effects on the methanol oxidation and possibilities for optimization should be explored in another study.

8.7 Discussion of the electrolyte's influences on the methanol oxidation

Previous experiments studied the influence of different supporting electrolytes on the product distribution of electrochemical methanol oxidation. Among others, different electrolyte compositions and concentrations were investigated and their physical and chemical properties were contextualized with the reaction's selectivity to formaldehyde. The methoxide and KOH experiments showed the largest difference on the product distribution depending on the supporting electrolyte concentration. At high concentrations, large quantities of formic acid formed, which was not observed for the perchlorate electrolytes. The main difference between methoxide and KOH compared to perchlorate electrolytes is the alkalinity, which becomes more pronounced at high concentrations. Yet, the exact influence of the alkalinity on the reaction pathways remained unclear.

The possible reaction pathways of methanol oxidation to formic acid are shown in Figure 8.18.^[98] Two possible reaction pathways include the formation of formaldehyde via initial C–H followed by O–H bond cleavage or vice versa (blue). One possible reaction pathway does not go via a formaldehyde but the first C–H bond cleavage is directly

followed by a second one (orange). If formaldehyde is formed, it can react further via a subsequent OH addition (green) or C–H bond cleavage (cyan) to H_2COOH and CHO , respectively. Other possible oxidation products can be CO and CO_2 if OH/OH^- is present (Figure 2.5, section 2.3). Please note that this graph shows the reaction with formally uncharged OH species as the reaction is assumed to take place with adsorbed OH.

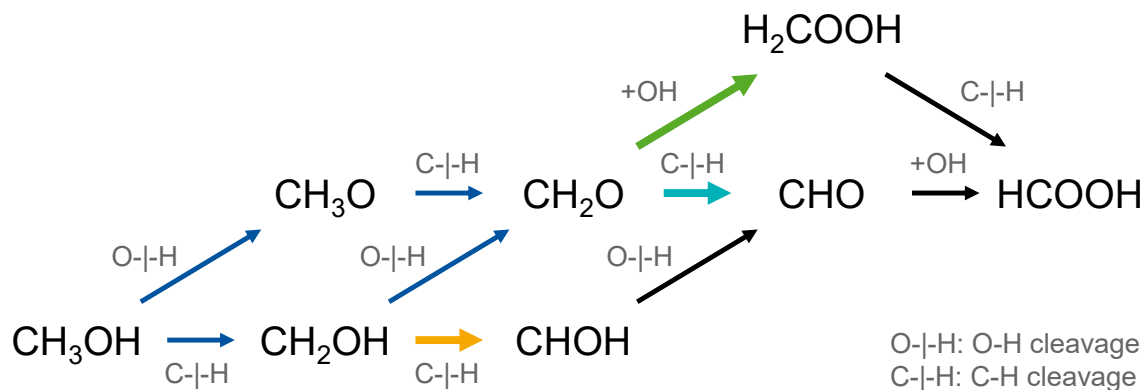


Figure 8.18: Schematic representations of the reaction pathways of the methanol oxidation that lead to formaldehyde (blue) and formic acid (black). The second C–H bond cleavage starting with methanol is highlighted orange. After formaldehyde formation, the subsequent reactions are OH addition (green) and C–H bond cleavage (cyan). Adapted from Ferrin *et al.*^[98]

To analyze the electrolyte's influence on the occurring reaction pathways, the Faraday efficiencies and conversions for formaldehyde and formic acid in different electrolytes (NaOMe , NaClO_4 and KOH) and electrolyte concentrations (0.1 mol L^{-1} and 1.0 mol L^{-1}) are discussed. The current density variation for 0.1 mol L^{-1} NaOMe (Figure 8.6) shows that the Faraday efficiency for formaldehyde stays constant and the produced amounts of formaldehyde increase linearly with the current density. In contrast, the Faraday efficiency for formic acid decreases because the same amount of formic acid is produced despite the increasing current densities. These trends are in contrast to the standard enthalpies of formation ($\Delta_f H^0$) for both molecules. Here, $\Delta_f H^0$ is higher for gaseous formaldehyde ($-108.6 \text{ kJ mol}^{-1}$) than it is for gaseous formic acid ($-378.7 \text{ kJ mol}^{-1}$).^[55] Yet, formaldehyde is the main reaction product, which indicates that the reaction steps leading to formic acid are kinetically hindered (green, cyan, and orange, Figure 8.18). It is noteworthy that these kinetic hindrances are not overcome at higher cell potentials (e.g., 18 V at 100 mA cm^{-2}) indicating that the formic acid formation is not limited by overpotential. Instead, a high alkalinity of the electrolyte can overcome the kinetic hindrance, which was shown by experiments with high concentrated NaOMe and KOH (section 8.3). In 1.0 mol L^{-1} NaOMe and KOH ,

the product distribution shifts towards formic acid but not in NaClO_4 . The KOH containing electrolyte supplies hydroxide anions that can facilitate the OH addition to formaldehyde enabling subsequent oxidation to formic acid (Figure 8.18 green). This indicates that one limiting factor for the formation of formic acid is the OH availability. While the substrate limitation can explain the product shift to formic acid for KOH, the same logic cannot be applied to NaOMe. Both electrolytes are alkaline but only KOH supplies direct OH^- . Nevertheless, the product distribution of NaOMe is similar to the one obtained with KOH. As less formaldehyde is formed in these highly alkaline electrolytes, it is possible that the alkalinity enables the C–H bond cleavage or hinders the O–H bond cleavage of methanol. In both cases, the orange path via CHOH (Figure 8.18) would become more dominant. To form formic acid from CHOH, the O–H bond has to be broken followed by an OH addition. If in these alkaline conditions the C–H bond cleavage is favored over the O–H ones, it should be more likely that CHOH also reacts via a third C–H bond cleavage to COH. The reaction products would then be CO or CO_2 after the addition of OH (Figure 2.5).^[98] However, this is not observed in the experiment as the sum of the Faraday efficiencies for formaldehyde and formic acid is $>90\%$.

In a methoxide electrolyte, it is possible that not methanol is involved in the oxidation reaction but its methoxide anion (OMe^-) reacts instead as a methanol that is already deprotonated at the oxygen. Starting from methoxide, formaldehyde is obtained after one C–H bond cleavage. If the C–H bond cleavage becomes more favored at high alkalinity (cyan reaction path, Figure 8.18), then formaldehyde is likely oxidized further. Alternatively, it is possible that a high NaOMe concentration facilitates the OH addition to formaldehyde (green path). The experiments were open to the atmosphere so water can diffuse into the solution. In contact with water, NaOMe forms MeOH and NaOH, which can then supply OH similar to KOH. This reactivity is more likely in concentrated, and thus, highly hygroscopic NaOMe electrolytes.

It is noteworthy that the experiments with high NaOMe concentrations primarily had high Faraday efficiencies for formic acid in the initial hours of the experiment. At longer reaction times (~ 15 h), the selectivity shifts towards formaldehyde (see also section 8.6). This selectivity change indicates that the dominant reaction pathway varies during the reaction. It is possible that a OH providing substance is consumed.

The concentration influence on the formaldehyde formation was only observed for the alkaline electrolytes NaOMe and KOH but not for the neutral NaClO_4 . For the latter, the Faraday efficiency for formaldehyde stayed constant regardless of the concentration, which allows a few hypothesis for its reaction influence:

1. The concentrated NaClO_4 electrolyte might be less hygroscopic than NaOMe , so no formic acid forms due to OH substrate limitations.
2. Because of its neutral pH properties, the C–H bond cleavage may not become favored so the oxidation is kinetically interrupted after the formation of formaldehyde.
3. The reaction proceeds via different favored reaction pathways.

The hypothesis for entirely different reaction mechanisms for NaOMe and NaClO_4 is supported by experiments applying different current densities. In 0.1 mol L^{-1} NaOMe , the amounts of produced formic acid remained constant independent of the applied current density. In 0.1 mol L^{-1} NaClO_4 , however, the amounts of formic acid increases ~ 5 times while the current density increases 10 times. It is possible that the OH addition, which is necessary for the formation of formic acid, is more likely to occur in neutral NaClO_4 than it is in alkaline NaOMe . The different formation behaviors for formic acid indicate that other reaction pathways are favored depending on the supporting electrolyte.

Despite the different reaction pathways, both methoxide and perchlorate electrolytes favor the formaldehyde formation at low concentrations. One possible reason for the high selectivity may be an initial O–H bond cleavage so the oxidation always proceeds via formaldehyde. Yet, the O–H bond cleavage is facilitated differently depending on the ion-interactions of the supporting electrolyte. In an methoxide electrolyte, the methoxide has a high electron density that can interact with the hydrogen of a methanolic O–H group weakening the O–H bond strength. In contrast, the perchlorate anion is a non-coordination anion that only weakly interacts with other species. Thus, the perchlorate supporting electrolyte is expected to be highly dissociated, which is also reflected in the high conductivity. Because the perchlorate has only a weak interaction with its cation, the cation can coordinate to the oxygen of methanol to weaken the O–H bond strength.

It is possible that the subsequent oxidation that is facilitated by the high alkalinity of the methoxide electrolytes is further enabled by their high viscosities. The influence of the viscosity should also be studied. The exact interaction of the supporting electrolyte with the methanol formation should be investigated in a future study.

The formation of formaldehyde is a kinetically controlled reaction. Based on thermodynamics, subsequent oxidation products (formic acid, CO ($\Delta_f H^0 = -110.5 \text{ kJ mol}^{-1}$),^[55] CO_2 ($\Delta_f H^0 = -393.5 \text{ kJ mol}^{-1}$)^[55]) are favored. Yet, formaldehyde is obtained as the

main product, which indicates kinetic barriers to subsequent reaction steps. The kinetic barriers for the oxidation can be overcome by multiple factors: The OH substrate limitation can be overcome by using hydroxide salts as supporting electrolytes. It also is possible that a hygroscopic electrolyte can supply enough water to produce the required OH^- in small scale setups. A high alkalinity might favor the C–H bond cleavage so formaldehyde is oxidized further, followed by OH^- addition to produce formic acid. As mentioned previously, formaldehyde can also be reduced to methanol, which is thermodynamically favored ($\Delta_f H^0 = -239.9 \text{ kJ mol}^{-1}$ [55]). Even though subsequent oxidations appear kinetically hindered, this might not apply to the formaldehyde reduction. Thus, a more in-depth investigation of the reaction mechanism and the electrolyte influences would be interesting. The chance of formaldehyde reduction can be minimized by separating anolyte and catholyte. To investigate the effect of a possible OH^- substrate limitation, the reaction has to be repeated in a closed system with dried NaOMe in methanol electrolytes. If the product distribution changes under completely anhydrous conditions, the hygroscopic properties of NaOMe-, KOH-, and NaClO_4 electrolytes should be investigated. If the product distribution does not change with the exclusion of OH^- , mechanistic insight and the likelihood of individual bond cleavages can be obtained by quantum mechanical calculations for electrolytes with different alkalinities. This should provide further insight into the alkalinity vs substrate limitation behavior, which would then also allow further insights in the reactivity of NaClO_4 .

9 Investigations of the reaction mechanism

In the previous chapter, the electrolyte's influence on the methanol oxidation reaction was discussed and how it can shift the product selectivity. But there are other parameters that also influence the reaction mechanism. In H-cell experiments (chapter 6), it was found that the selectivity of the formaldehyde formation on Pt is also influenced by the applied potential. Low potentials yielded some formaldehyde, medium potential resulted in no current flow and the highest applied potential achieved the highest selectivity to formaldehyde. Therefore, the potential dependent product distribution for NaOMe electrolytes was investigated in more detail in the flow cell. Different current densities were applied to relate to the H-cell experiments.

The electrolyte investigation (chapter 8) also found different reaction behavior for NaOMe and NaClO₄. To gain a better understanding of the methanol oxidation and how it is influenced by the two supporting electrolytes, the surface species during the electrochemical oxidation were analyzed.

9.1 Potential influence on the reaction mechanism

H-cell CVs in 0.1 mol L⁻¹ NaOMe (Figure 6.1 a), see also chapter 6) showed two oxidation peaks at 0.7 V and 1.3 V vs fc followed by an increasing current response at potentials >1.5 V vs fc. Measuring a CA at the peak maxima showed distinct current responses and product distributions indicating that different reactions occur at each potential. Thus, it was investigated whether similar behavior can be observed in the flow cell. The Faraday efficiencies were determined for NaOMe, NaClO₄ and LiClO₄ after applying different current densities for 30 min (Figure 9.1) and the Faraday efficiency trends for NaOMe are compared to the H-cell results. The current density 10 mA cm⁻²

relates to the one measured in the H-cell setup at 0.7 V vs fc. For additional references, a lower (4 mA cm^{-2}) and a higher current density (100 mA cm^{-2}) was applied.

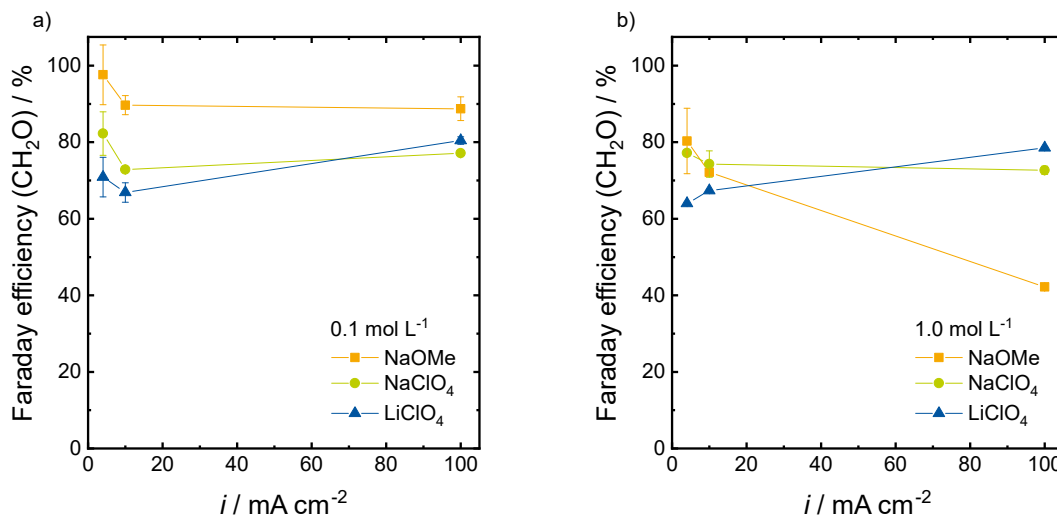


Figure 9.1: Faraday efficiency for formaldehyde of a) 0.1 mol L^{-1} and b) 1.0 mol L^{-1} at 4 mA cm^{-2} , 10 mA cm^{-2} and 100 mA cm^{-2} . The experiments were performed on Pt for 30 min with 40 mL electrolyte that was recirculated with 100 mL min^{-1} .

All electrolytes with a concentration of 0.1 mol L^{-1} (Figure 9.1 a)) show a similar behavior with a drop in the Faraday efficiency after increasing the current density from 4 mA cm^{-2} to 10 mA cm^{-2} . Increasing the current density further has no effect on the Faraday efficiency for NaOMe and NaClO_4 , but it increases for LiClO_4 .

In 1.0 mol L^{-1} , the Faraday efficiency decreases for NaOMe and NaClO_4 when the current density is increased from 4 mA cm^{-2} to 10 mA cm^{-2} . Afterwards, it stays constant for NaClO_4 while it decreases for NaOMe. For LiClO_4 , the Faraday efficiency increases with increasing current density.

The largest differences in the behavior are observable for NaOMe. Applying a low current density yields the highest Faraday efficiencies for both concentrations. This behavior corresponds to the one observed in the H-cell. At low current densities (4 mA cm^{-2}), the reaction might perform according to the reaction observed at 0.7 V vs fc, whereas at current densities $>10 \text{ mA cm}^{-2}$, the reaction mechanism observed at 2.4 V vs fc prevails. At 10 mA cm^{-2} , the Faraday efficiency drops similarly though not as extensively as it was observed in the H-cell at 1.3 V. The efficiency loss might be caused by oxidation to CO and subsequent electrode poisoning due to CO adsorption.

The varying reaction behavior at the two NaOMe concentrations indicates a concentration dependency of the reaction mechanism. In 0.1 mol L^{-1} , the selectivity decreases

when the current density is increased from 4 mA cm^{-2} to 10 mA cm^{-2} . But the reaction remains robust when the current density is increased further. In 1.0 mol L^{-1} , the Faraday efficiencies at 4 mA cm^{-2} and 10 mA cm^{-2} are lower by 17 pp. compared to the 0.1 mol L^{-1} electrolyte solution. However, with increasing current densities the Faraday efficiency drops further (see also section 8.3 for a more detailed discussion). In contrast, the performance in NaClO_4 appears independent from the current density for both concentrations, and thus, it is likely that the reaction mechanism does not change with the potential/current. The trends for LiClO_4 are ambiguous, but the overall behavior seems to resemble that of NaClO_4 .

The differences in the selectivity can also be caused by different Pt-oxides present on the anode. Because of the low electrode potentials at 4 mA cm^{-2} , it is possible that the reaction occurred on elemental Pt. At 10 mA cm^{-2} , Pt-oxides might have formed that have a different selectivity for the methanol oxidation. It can be safely assumed that at 100 mA cm^{-2} , mainly PtO_2 is present on the electrode surface. The oxygen required for the Pt oxidation can be supplied by trace amounts of water (0.1-0.2 wt%) as well as dissolved oxygen. The effect of the potential on the platinum oxidation was discussed in more detail in chapter 6. Thus, material changes can cause changes in current/potential behavior during the electrooxidation of anhydrous methanol. Other processes such as CO formation that blocks Pt sites as a strongly bound intermediate can also be responsible for the current drop.

There seems to be an additional interplay with NaOMe electrolytes and the cell potential. Repeated measurements at the different current densities lead to varying cell potentials by up to 50 % despite identical reaction conditions (Figure A.13), which was not observed for other supporting electrolytes. This varying-potential phenomenon was repeatedly observed for other NaOMe experiments. Cell reassembly, with or without electrode cleaning as well as electrolyte exchange were not reproducibly able to force one cell potential, regardless of it being the higher or lower one. No correlation was found compared to any experimental quantity and it remained unknown what causes these potential differences. To understand this behavior, a systematic investigation is required. The cell potentials of the NaOMe experiments that were used for the calculation of the specific energy consumption were averaged over the measurements, which sometimes causes larger error bars.

9.2 ATR-SEIRA spectroscopy and surface species analysis

The potential dependent measurements show different reaction behaviors for NaOMe and NaClO₄. For an in-depth understanding on how the electrolyte affect the reaction mechanism, it is vital to know about the surface species on the catalyst as well as reaction intermediates. For that purpose, attenuated total reflection surface-enhanced infrared adsorption spectroscopy (ATR-SEIRAS) was performed to study *in-situ* formed surface species, e.g. OMe and CO, on the Pt anode. For the electrooxidation of methanol, a potential of 2.4 V vs fc was applied to pure methanol and methanolic NaOMe (0.1 mol L⁻¹ and 1.0 mol L⁻¹) (Figure 9.2). Other maximum peak potentials (0.7 V and 1.3 V) were also investigated, but the spectra did not change with respect to the potential (Figure A.14). It was noted in the literature that the IR baseline can be shifted and distorted by an electric field.^[189] Thus, the peak intensities or changes are not analyzed and only the peak appearance is discussed.

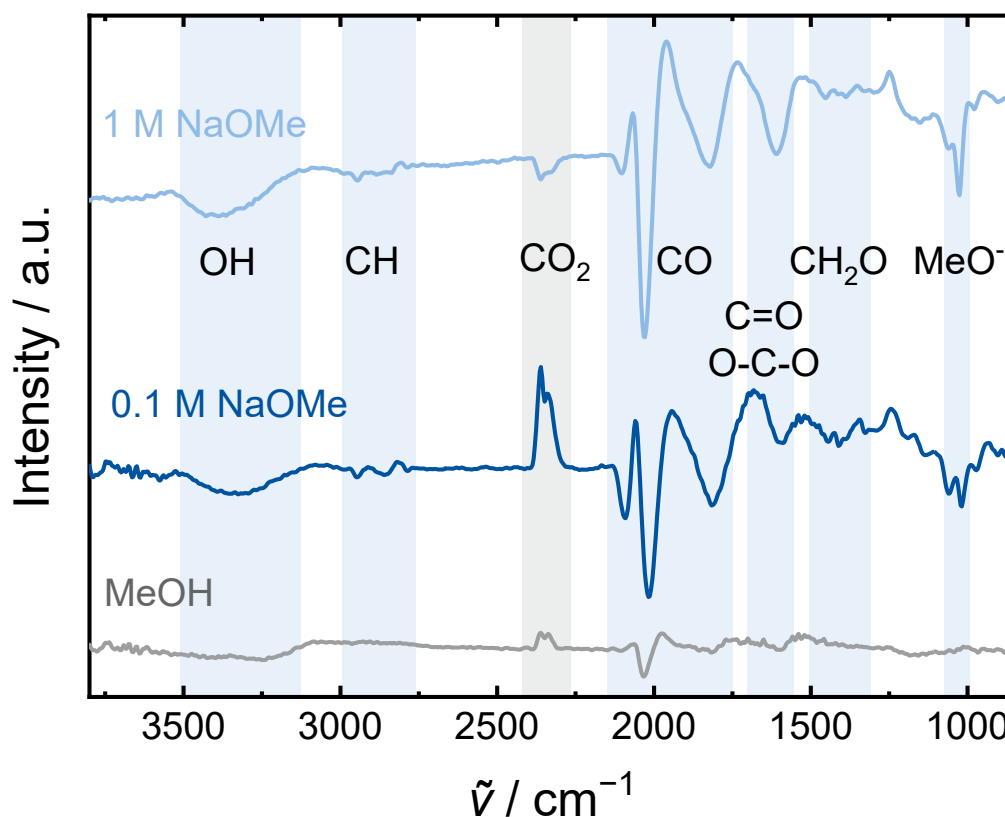


Figure 9.2: ATR-SEIRA spectra of methanol and 0.1 mol L⁻¹ and 1.0 mol L⁻¹ solution of NaOMe in methanol recorded on a Pt thin film electrode in the ATR-cell at 2.4 V vs fc.

All electrolytes show a vibration band in the range of $3500\text{--}3100\text{ cm}^{-1}$ that is characteristic for O–H stretching of methanol.^[190] The spectra in NaOMe solution shows two additional bands at 2940 cm^{-1} and 2845 cm^{-1} that can be attributed to the C–H stretching band of CH_3 of methanol or methoxy species.^[190,191] All three spectra show a band around 2350 cm^{-1} that is characteristic for CO_2 .^[191] This band is marked in gray as it cannot be analyzed. The experimental setup was open to the atmosphere, and thus, any determined CO_2 near the surface can also originate from the surrounding air. Strong vibration bands around 2025 cm^{-1} and 1815 cm^{-1} indicate the presence of both linearly and bridged/multiply bound CO.^[192–195] The band around 1700 cm^{-1} can be ascribed to a carbonyl species (e.g., formaldehyde).^[191] It overlaps with an adsorbed HCO species (1660 cm^{-1})^[196] and the O–C–O stretching vibration of dissolved formate ($1610\text{--}1590\text{ cm}^{-1}$).^[191] A vibration band between $1470\text{--}1430\text{ cm}^{-1}$ attributed to a $-\text{O}-\text{CH}_2$ species suggests adsorbed formaldehyde or methylene glycol.^[197] In the same frequency range is the symmetric and asymmetric CH_3 bending vibration ($1480\text{--}1420\text{ cm}^{-1}$) and O–H in-plane bending vibration (1420 cm^{-1}) of adsorbed methanol.^[190] The C–O stretching vibration of methanol, methoxy, methyl formate and formaldehyde is observable between $1070\text{--}1010\text{ cm}^{-1}$.^[190,192,198]

Other bands that are not highlighted in Figure 9.2 are a O–C–O stretching vibration of bidentate formate ($1320\text{--}1274\text{ cm}^{-1}$)^[191,192,195,196] and the C–O stretching vibration of formic acid in solution ($1220\text{--}1150\text{ cm}^{-1}$).^[192]

No significant differences can be seen for the surface species for both NaOMe concentrations. In methanol, only CO and CO_2 can be observed on the surface. The lack of presence of O–H or CH_3 bands indicate that in pure methanol no reaction occurs at the applied potential and the supporting electrolyte is required for methanol activation. As no other surface species are detected, it is possible that CO was still adsorbed on the surface from a previous experiment. Because of the strong adsorption of CO on Pt, it may not have been removed by the electrode cleaning via methanol rinsing.

Although ATR-SEIRAS is an impactful technique to determine surface active species and intermediates, a clear differentiation in case of the methanol oxidation is difficult. One reason for this are the overlapping vibration bands due to the similarity of surface-near species. In addition, band positions are influenced by the electric field. It can be safely assumed that a methoxy species is present on the surface due to multiple ATR-SEIRA signals. The methoxy species can originate from the supporting electrolyte or from methanol after an initial O–H bond cleavage. The presence of a O–H stretching band indicates that a CH_2OH species is adsorbed on the surface originating from an initial C–H bond cleavage of methanol. Thus, no clear statement can be made whether

an initial C–H bond cleavage occurs. The methanol oxidation in methanolic NaOMe proceeds at least via initial O–H bond cleavage and the impact of initial C–H cleavage needs to be investigated in the future. No conclusive statement for the dominant reaction path can be made.

In the electrolyte study, it was found that the reactivity in NaOMe differs strongly from the one in NaClO₄ electrolytes, which indicates a different reaction path. Therefore, the surface species in an 0.1 mol L^{−1} NaClO₄ electrolyte were also determined via ATR-SEIRAS, and the spectrum is shown in Figure 9.3.

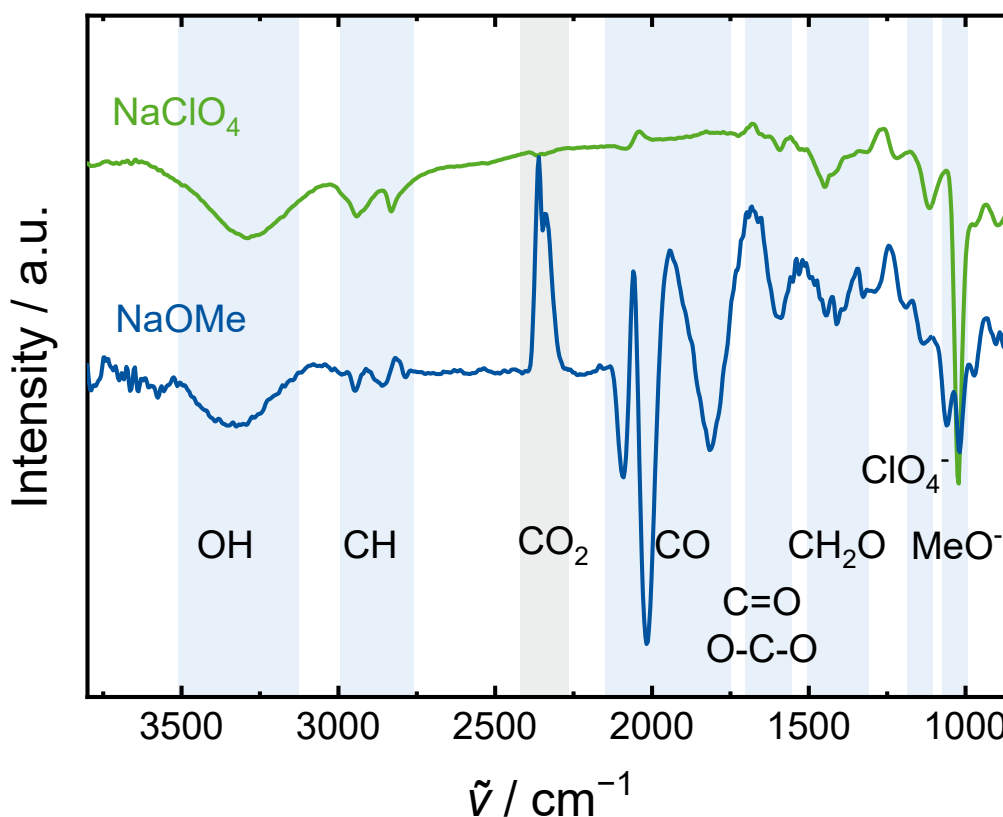


Figure 9.3: ATR-SEIRA spectra of 0.1 mol L^{−1} NaOMe and NaClO₄ in methanol recorded on a Pt thin film electrode in the ATR-cell at 2.4 V vs fc.

The spectrum obtained in methanolic 0.1 mol L^{−1} NaClO₄ contains many similarities to the one measured in NaOMe. Both spectra show O–H stretching vibration of methanol (3500–3100 cm^{−1}),^[190] C–H stretching vibrations of methanol and methoxy (2940 cm^{−1} and 2845 cm^{−1}),^[190,191] –O–CH₂ of (oxygen bound) formaldehyde and methylene glycol (1470–1430 cm^{−1}),^[197] C–H bending frequencies of methanol and methoxy (1480–1420 cm^{−1}),^[190] O–H in-plane bending of methanol (1420 cm^{−1}),^[190] O–C–O stretching of bidentate formate ((1320–1274 cm^{−1}, not highlighted),^[191,192,195,196]

and C–O stretching of methanol, methoxy, methyl formate and formaldehyde ($1070\text{--}1010\text{ cm}^{-1}$).^[190,192,198] The NaClO_4 spectrum provides an additional band at 1100 cm^{-1} that can be ascribed to ClO_4^- .^[192] This peak might overlap with the C–O stretch frequency of formic acid in solution ($1220\text{--}1150\text{ cm}^{-1}$).^[192]

The main differences between the spectra of both electrolytes are the lack of CO bands as well as the missing band between $1700\text{--}1590\text{ cm}^{-1}$ in NaClO_4 . In this range, typically carbonyl species,^[191] such as deprotonated formaldehyde (HCO),^[196] can be observed as well as the O–C–O stretching frequency of dissolved formate.^[191] In aqueous media, HCO is a shared intermediate of the electrochemical oxidation of methanol and formaldehyde on the path to CO.^[199] No HCO band is found on the Pt electrode, which indicates that CO is not formed in NaClO_4 . Instead, formaldehyde is oxidized either to formic acid or CO_2 . The absence of CO formation in NaClO_4 suggest less electrode poisoning. However, in 0.1 mol L^{-1} concentrations, NaOMe as the supporting electrolyte provides a higher Faraday efficiency to formaldehyde than NaClO_4 implying other occurring side reactions in NaClO_4 instead of the CO formation.

Both supporting electrolytes have similar pre-formaldehyde surface species as indicated by adsorbed methoxy- and CH_2OH intermediates. No definitive statement can be made whether an initial C–H or O–H bond cleavage is preferred. Nevertheless, the tested electrolytes differ in the post-formaldehyde-oxidation products as CO is only present on the surface in NaOMe while NaClO_4 yielded higher formic acid concentrations. It is possible that in the alkaline NaOMe the C–H bond cleavage is more likely to occur than in a neutral environment (cyan and orange Figure 8.18). If the C–H bond cleavage is also more favored than the OH addition, formaldehyde is rather oxidized to CO than formic acid. The different surface species in the two electrolytes corroborate that the reaction proceeds via different reaction pathways. The exact influence of the electrolyte requires further investigations.

10 Conclusion

Formaldehyde is an important C1 building block in the chemical industry. The electrification of its synthesis could represent a step toward a more sustainable process. This work investigated the scalability of the electrochemical methanol oxidation to formaldehyde to industrial application and how individual reaction parameters affect the process. To identify active electrode materials, a suitable reference electrode (RE) was developed and used to measure the activity of various electrode materials. Promising electrodes were then transferred to a flow cell and investigated for their scalability regarding electrode size and applied current density. The scale-up also affects several setup parameters that influence the methanol oxidation, and their impact was analyzed. For a better understanding of the methanol oxidation, an in-depth study was conducted on the influence of the electrolyte composition on the reaction mechanism. A RE is required to accurately describe electrode activity and stability. For use in anhydrous reaction environments, Ag/Ag⁺ REs are often used. The potential of these reference electrodes is affected by liquid junction potentials that depend on the solvent and ions present. Thus, the influence of different ions in the RE filling solution and the electrochemical cell was studied for methanol-based Ag/Ag⁺ REs because differing ions present can cause liquid junction potentials (LJPs) (*Research Question 1*). These LJPs shifted the RE potential by up to 50 mV depending on the ion combination of the RE filling solution and the cell electrolyte. Although the Ag/Ag⁺ REs provide stable potentials depending on the ion combination, they are only short-term stable. To improve stability, anhydrous methanol-based Ag/AgCl REs were constructed (*Research Question 2*) and their characteristics compared with literature-reported REs (*Research Question 3*): an aqueous methanol Ag/AgCl, the previously mentioned methanol-based Ag/Ag⁺ and a Ag wire. The developed methanol-based Ag/AgCl REs allow accurate potential measurements vs ferrocene for multiple weeks, but their impedance is too high for precise electrochemical impedance spectroscopy (EIS). The Ag wire requires daily potential determination but is recommended for EIS.

The methanol-based Ag/AgCl REs were used for CV studies of Pt, Cu, Ni, Ag, and Au for the oxidation of methanol in an H-cell (*Research Question 4*). Pt, Au and Ni were active for the oxidation of methanol to formaldehyde while Cu and Ag either showed low activity or were unstable under these conditions. The active materials were investigated in industrially more relevant conditions in a flow cell (*Research Question 5*). Here, the electrode was scaled up to 12 cm^2 , the electrolyte volume was reduced, and the system was simplified to a two-electrode setup. In the scaled-up flow cell, Pt, Au and Ni plate electrodes were investigated across a range of current densities. Ni and Au appear to be unstable at higher current densities, and the selectivity of Au shifted toward formic acid as the main reaction product. Remarkably, the Pt WE was stable at high cell potentials and current densities with Faraday efficiencies for formaldehyde of up to 90 %. Because of its stability and selectivity, the Pt WE allowed an increase to industrially relevant current densities of up to 100 mA cm^{-2} .

Not only was the scalability of the WE was investigated, but also the influence of the flow cell reaction parameters (flow rate, electrode gap, temperature) and their interplay with the applied current densities (*Research Question 6*). A high flow rate was found to favor the formaldehyde formation indicating that a fast removal of formaldehyde is essential to avoid subsequent formaldehyde oxidation. The influence of the electrode gap on the Faraday efficiency is ambiguous, but it heavily influences the specific energy consumption (E_s). Because of the poor conductivity of methanol-based electrolytes, a smaller electrode gap significantly reduced the required cell potential. Adding external heating or cooling to the electrolyte had only a minor influence on the Faraday efficiency. For further scale-up, fast mass transport, a heated electrolyte reservoir, and a small electrode gap are recommended.

The effects of the electrolyte composition and its properties on the formaldehyde formation were investigated through a supporting electrolyte screening and a systematic study of NaOMe, LiOMe, NaClO₄, and LiClO₄ (*Research Question 7-9*). The acid-base properties of the supporting electrolyte were found to have the main influence on the reaction mechanism. Acidic supporting electrolytes did not yield formaldehyde, in contrast to neutral and alkaline ones. In low-concentration methoxide electrolytes, the amount of formed formaldehyde increases linearly with the current density while the amount of formic acid remains nearly constant. According to their standard enthalpy of formation, formaldehyde is the least favored reaction product compared to formic acid, CO, and CO₂ indicating that formaldehyde is not oxidized further due to kinetic limitations. It was previously found that a higher flow rate yielded higher Faraday efficiencies for formaldehyde. This correlation denotes that the formaldehyde forma-

tion is primarily mass-transport limited in the current setup while the other reactions are likely restricted by reaction kinetics. Further study is required to analyze how the viscosity impacts the mass transport and, in turn, affects subsequent oxidation.

At high alkalinity, the primary reaction pathway during the electrochemical reaction shifts from producing formaldehyde to formic acid. It remains unclear whether high alkalinity enables the subsequent oxidation of formaldehyde or the formic acid formation proceeds via a formaldehyde-omitting pathway. Since formaldehyde remains the main reaction product, it seems likely that the kinetic barrier for the subsequent formaldehyde oxidation is lowered. A major influence of the supporting electrolyte on the occurring reaction mechanism is also supported by ATR-SEIRAS measurements during the electrochemical reaction because adsorbed CO was only found for NaOMe but not for NaClO₄.

The viscosity of the electrolytes inversely correlates with conductivity as more viscous electrolytes are less conductive. However, the cell potential is similar for concentrated methoxide and perchlorate electrolytes despite different conductivities, which indicates an additional, yet unknown, effect on the cell potential. The electrolyte resistance can be estimated by taking the conductivity and the electrode gap into account. The corrected cell potentials show a different behavior for the methoxide and perchlorate electrolytes independent of the investigated cations. For methoxide electrolytes, the corrected cell potentials are independent of the electrolyte concentration while they increase with concentration for perchlorate electrolytes. The cause of these differing behaviors remains ambiguous, but it emphasizes the influence of the supporting electrolyte on the reaction mechanism. The physical properties of the tested electrolytes are mainly characterized by the anion of the supporting electrolyte; thus, varying anions have a major influence on the reaction performance. For the cation, it was found that larger alkali cations favor the formaldehyde formation. Alkali metals become more reactive and their cations more stable with increasing atomic number. It is unclear whether alkali metal properties, e.g., low ionization energy and low electronegativity, or the cation size benefit the formaldehyde formation. Mixing different supporting electrolytes was investigated to tailor electrolyte properties. The E_s of a low-conductivity supporting electrolyte can be lowered by adding conductivity agents while maintaining high Faraday efficiencies. Still, a conductivity threshold is reached where the cell potential stays constant despite adding more conductivity agent. At the threshold, the cell potential is defined by kinetic overpotentials. No improvement in the Faraday efficiencies or E_s was observed by adding NaClO₄ to highly alkaline electrolytes.

To facilitate the formaldehyde formation, the ideal electrolyte eases the O–H bond cleavage, because the methanol oxidation then always proceeds via formaldehyde. Alkaline electrolytes might influence the reaction mechanism by supplying anions interacting with the O–H functionality of methanol and thereby ease the O–H bond cleavage. In contrast, perchlorate as a stable, non-coordinating anion allows its cation to coordinate to the oxygen of methanol facilitating an easier deprotonation. If a suitable electrolyte is found that supports the O–H bond cleavage, the electrode activity can be optimized for single C–H bond cleavage to form formaldehyde while avoiding subsequent oxidation by additional C–H bond cleavage.

Overall, these results show that the electrooxidation of anhydrous methanol to formaldehyde can successfully be scaled-up to approach industrial application. Transferring the reaction into a flow cell setup shows a beneficial impact of the mass transport on the formaldehyde selectivity. The formaldehyde formation is scalable by at least one order of magnitude in both electrode size and applied current densities. Both are vital parameters for a successful industrial application as they determine the formaldehyde formation rate. For further understanding of the methanol oxidation, a more in-depth study of the electrolyte influence revealed a high sensitivity to the electrolyte composition. The supporting electrolyte determines the occurring reaction mechanism and, thus, the product distribution. Though both ions of the supporting electrolyte contribute to the reaction mechanism, the major influence is the alkalinity. These insights enable the tailoring of an electrolyte composition beneficial for the formaldehyde formation.

In conclusion, this work provides a basis for the potential electrification of the formaldehyde synthesis via anhydrous methanol oxidation. The reached current densities are industrially relevant, and they can easily be increased further along with the electrode size to achieve industrially applicable conversion. The main limiting factor for industrial application is the high energy requirement, which can be lowered by improving the reactor design and electrolyte conductivity. Further improvements can be made by lowering the overpotential of the electrode material for the formaldehyde formation. To reduce the investment costs, non-noble electrode materials or lower Pt loadings can be investigated. Thus, further scale-up of the electrification of the formaldehyde synthesis is feasible for industrial application but more research is required.

11 Outlook

In this work, some understanding about the reaction mechanism of the oxidation of anhydrous methanol and its dependency on the electrolyte composition was gained. However, deeper knowledge is required to further improve the reaction performance. It was found that the E_s can be lowered by adding conductivity agents to low conducting electrolytes, and thus the cell potential is directly linked to the electrolyte composition. To understand the interplay between the electrolyte and the formaldehyde formation, further investigations are required. One possible approach is the use of a rotating ring disk electrode with a constant rotation for a steady mass transport. This enables a more accurate investigation of the electrochemical reaction. Varying the rotation rate also allows an isolated study of the mass transport's influence. A high rotation rate and thus, fast mass transport, is expected to favor the electrochemical formaldehyde formation in anhydrous methanol. Comparing the formaldehyde formation of different supporting electrolytes at different concentrations may provide understanding of the occurring overpotentials. The overpotential and its causes are closely linked to the reaction mechanism.

To fully understand the occurring reactions, all of the reaction products need to be accounted for. To close the mass balance, the cell and the periphery should also be made gas tight to allow a proper detection of gaseous products. The tight cell has the additional benefit that the hygroscopic properties are less influential and it can be studied whether this influences the formation of formic acid. Knowledge about the possible and probable reaction paths allows one to tailor the conditions benefiting the formation of formaldehyde while avoiding side- and subsequent formaldehyde reactions. The experiments showed that the formaldehyde formation is kinetically favored and it is expected that high temperatures benefit the reaction kinetics. A heat insulation for the cell and the periphery allows for a more accurate temperature control to accurately investigate the temperature influence on the reaction kinetics. To study higher temperatures, the oxidation of gaseous anhydrous methanol might be worth investigation. As formaldehyde is the kinetic reaction product, subsequent oxidation at the

anode or reduction at the cathode is likely whenever formaldehyde is in contact with an electrode. With increasing methanol conversion, subsequent formaldehyde reactions become more likely, which lowers the reaction's selectivity. Thus, there is a trade-off between conversion and selectivity and it needs to be studied in more detail how they affect each other.

Understanding the correlation between conversion and selectivity of the formaldehyde formation can also lead to improved reactor designs. To improve the selectivity of the methanol oxidation, a separator can be introduced to the flow cell. Dividing anolyte and catholyte can reduce the chance of formaldehyde reduction. A suitable separator without methanol crossover can allow the use of a gas diffusion electrode (GDE) for the hydrogen evolution on the cathode side. To avoid selectivity losses at higher conversions, downstream options for the methanol formaldehyde separation can be investigated. One possibility can be the partial methanol conversion with a subsequent distillation of the reaction mixture and methanol recycling or an *in-situ* extraction of formaldehyde. The methanol can then be recycled while maintaining a high selectivity for formaldehyde. Achieving high conversions while maintaining a high selectivity can also be addressed by investigating different reactor types and modes of operation. For example, porous foam structure as the anode provides a high active surface area. The electrolyte flows through the foam and the current is pulsed, which oxidizes the majority of the methanol due to the high surface area. Further oxidation is avoided due to the current stop while the electrolyte is flushed out of the electrode structure. An improved reactor should also reduce the electrode gap to lower the cell potential. This can be achieved by introducing a separator and a GDE, which eliminates the need for a liquid electrolyte on the cathode side. The anodic electrode gap could be reduced by using a foam electrode, which could be pressed on the separator. As a foam electrode impedes the mass transport, it might enable further formaldehyde reactions. Then, a smooth surface with small distance to the separator should be preferred. These improved reaction conditions and reactor design can then be used for the next scale-up step to 100 cm² electrodes.

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A Appendix

A.1 Materials and methods

Table A.1: List of used instruments and their manufacturers.

Instrument	Supplier	Model
Conductometer	Metrohm	712
Gas chromatograph	Agilent	8860
Liquid chromatograph	Agilent	1160
IR spectrometer	Bruker	Vertex70
Kark Fischer coulometer	Metrohm	831
Peristaltic pump	Masterflex	L/S Digital Drive
Potentiostat	Gamry Instruments	1010E
Potentiostat	Gamry Instruments	Reference 3000
Pump head	Masterflex	L/S Easy-Load II
Rheometer	Anton Paar	MCR 102
Scanning electron microscope	Hitachi	TM3030
Tubing	Masterflex	C-Flex Ultra

LiOMe was stored at 4°C under nitrogen atmosphere to minimize degradation to avoid water diffusion. Most experiments in this work were carried out with methanol (2.5 L, 99.9 %) by Chemsolute after initial experiments with 1 L methanol flasks were successful. Once, methanol was ordered from Emsure with the same purity of 99.9 % due to faster delivery times. No experimental difference was found for the different suppliers.

Table A.2: Chemicals and their suppliers.

Name	Chemical formula	Supplier	Purity / %
Acetic acid	CH ₃ COOH	Chemsolute	100
Dipotassium phosphate	K ₂ HPO ₄	Supelco	99.5
Ferrocene	C ₁₀ H ₁₀ Fe	Merck	98
Hydrochloric acid	HCl	Emsure	37
Lithium chloride	LiCl	VWR Life Science	98
Lithium methoxide in MeOH	LiOMe	Aldrich	1 mol L ⁻¹
Lithium perchlorate	LiClO ₄	thermoscientific	98
Methanol (1 L)	MeOH	Chemsolute	99.9
Methanol (2.5 L)	MeOH	Chemsolute	99.9
Methanol (2.5 L)	MeOH	Emsure	99.9
Monopotassium phosphate	KH ₂ PO ₄	Supelco	99.5
Nitric acid	HNO ₃	Chemsolute	65
Phosphoric acid	H ₃ PO ₄	Carl Roth	70
Potassium hydroxide	KOH	Chemsolute	85
Potassium perchlorate	KClO ₄	thermoscientific	99
Silver nitrate	AgNO ₃	Alfa Aesar	-
Silver perchlorate	AgClO ₄	Alfa Aesar	99.9
Sodium methoxide (solid)	NaOMe	thermoscientific	98
Sodium methoxide in MeOH	NaOMe	thermoscientific	30 wt.
Sodium perchlorate	AgClO ₄	Alfa Aesar	98
Sodium <i>tert</i> -butoxide	NaOC(CH ₃) ₃	thermoscientific	99
Sodium sulfate	Na ₂ SO ₄	Carl Roth	98.5
Sulfuric acid	H ₂ SO ₄	Carl Roth	95
Tetrabutylammonium perchlorate (TBAP)	N(Bu) ₄ ClO ₄	Alfa Aesar	98

Table A.3: Electrodes and their suppliers.

Material	Supplier	Purity / %
Au foil (0.25 mm)	Evo Chem	99.9
Au wire (0.25 mm)	Goodfellow	99.99
Ag wire (0.50 mm)	Roth	99.9
Ag wire (RE-7N)	ALS	-
Carbon GDE	FuelCellStore	-
Cu wire (0.50 mm)	Goodfellow	99.95
Glassy carbon rod (1.00 mm)	HTW	-
Ni foil (1 mm)	Goodfellow	99.98
Ni wire (0.25 mm)	HMW Hauner	99.99
Pt foil (0.25 mm, 5x5cm)	Goodfellow	99.99+
Pt/C GDE	FuelCellStore	50 mg cm ⁻²
Pt (2.5 µm)/Ti (6x7cm)	Metakem	-
Pt wire (0.25 mm)	Goodfellow	99.99+

A.2 Investigation of water-free reference electrodes

A.2.1 Characterization and comparison of methanol based reference electrodes

Table A.4: Frequencies, impedances, resistances, reactances and phase angles of RE 1 on day 1, 2, 3, 6, 7.

Day d	Frequency Hz	Impedance Ω	Resistance Ω	Reactance Ω	Phase angle $^{\circ}$
1	444	25420	25420	158	-0.356
2	398	28117	28116	229	-0.467
3	398	26902	26901	241	-0.513
6	252	28243	28242	226	-0.458
7	352	27296	27295	248	-0.521

Table A.5: Frequencies, impedances, resistances, reactances and phase angles of RE 2 on day 1, 2, 3, 6, 7.

Day d	Frequency Hz	Impedance Ω	Resistance Ω	Reactance Ω	Phase angle $^{\circ}$
1	178	25879	25879	161	-0.356
3	445	27614	27613	229	-0.475
3	283	26840	26839	232	-0.495
6	352	27814	27813	227	-0.467
7	283	27239	27238	242	-0.509

Table A.6: Frequencies, impedances, resistances, reactances and phase angles of RE 3 on day 1, 2, 3, 6, 7.

Day d	Frequency Hz	Impedance Ω	Resistance Ω	Reactance Ω	Phase angle $^{\circ}$
1	316	26641	26640	196	-0.421
2	445	27556	27555	248	-0.516
3	564	26881	26880	276	-0.588
6	252	27731	27729	277	-0.573
7	352	27438	27437	279	-0.582

Table A.7: Frequencies, impedances, resistances, reactances and phase angles of RE 4 on day 1, 2, 3, 6, 7.

Day d	Frequency Hz	Impedance Ω	Resistance Ω	Reactance Ω	Phase angle $^{\circ}$
1	445	24542	24541	157	-0.366
2	496	25474	25473	212	-0.477
3	445	24538	24537	231	-0.540
6	398	24811	24809	244	-0.564
7	445	25191	25190	227	-0.516

Table A.8: Frequencies, impedances, resistances, reactances and phase angles of RE 5 on day 1, 2, 3, 6, 7.

Day d	Frequency Hz	Impedance Ω	Resistance Ω	Reactance Ω	Phase angle $^{\circ}$
1	891	16384	16383	181	-0.631
2	1397	16096	16095	209	-0.744
3	1397	16224	16223	214	-0.758
6	998	16235	16233	228	-0.805
7	998	16191	16189	232	-0.820

Table A.9: Frequencies, impedances, resistances, reactances and phase angles of RE 6 on day 1, 2, 3, 6, 7.

Day d	Frequency Hz	Impedance Ω	Resistance Ω	Reactance Ω	Phase angle $^{\circ}$
1	1127	15569	15569	163	-0.598
2	998	15380	15379	162	-0.603
3	998	15494	15493	181	-0.671
6	891	15450	15449	181	-0.670
7	891	15416	15415	180	-0.669

Table A.10: Frequencies, impedances, resistances, reactances and phase angles of RE 7 on day 1, 2, 3, 6, 7.

Day d	Frequency Hz	Impedance Ω	Resistance Ω	Reactance Ω	Phase angle $^\circ$
1	5016	101	101	9	-5.339
2	5016	83	82	11	-7.743
3	5016	85	84	14	-9.488
6	5016	91	90	12	-7.319
7	5016	70	69	13	-10.397

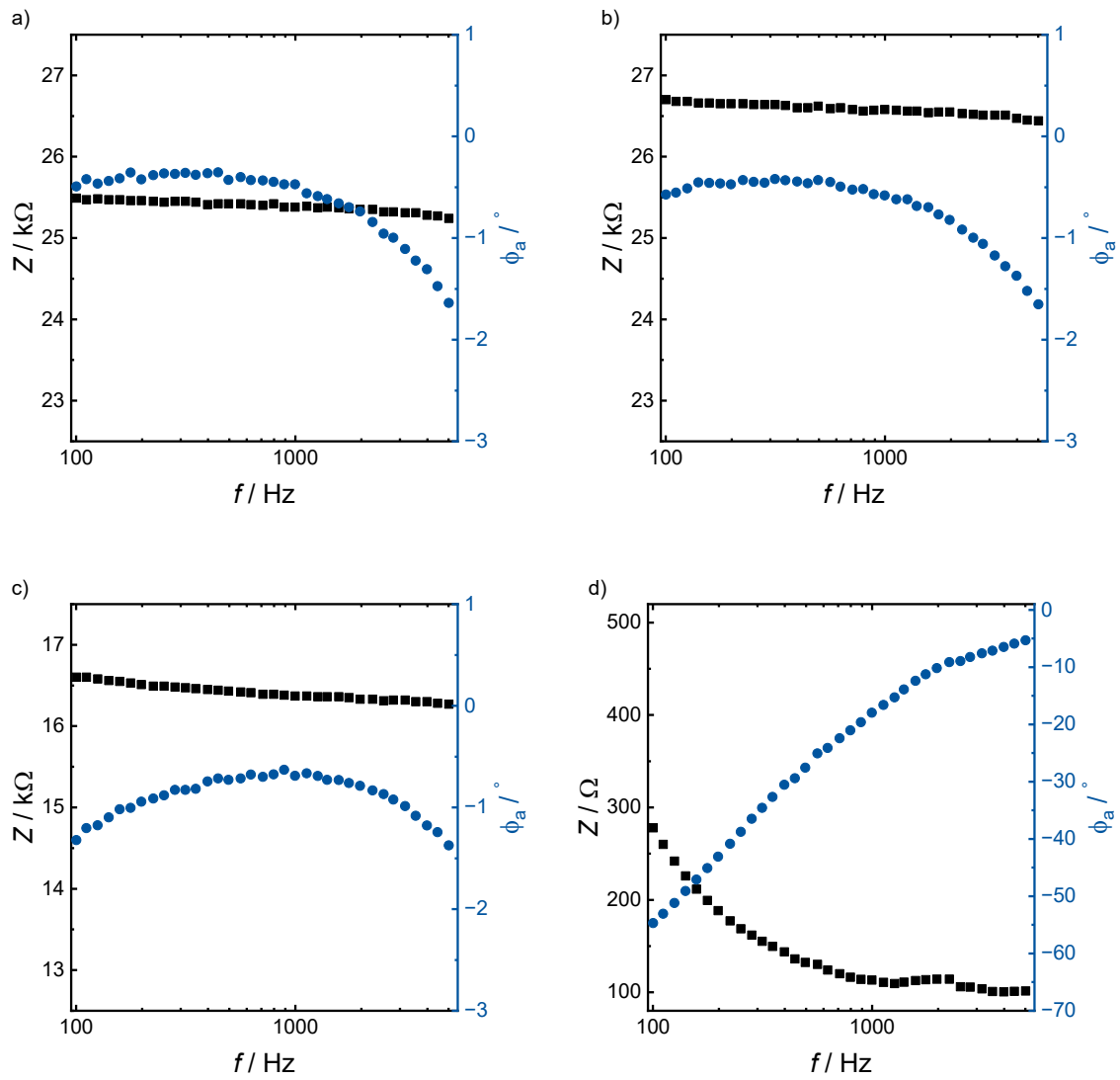


Figure A.1: Bode plots for a) RE 1, b) RE 3, c) RE 5 and d) RE 7.

A.3 Electrochemical oxidation of anhydrous methanol in a batch H-cell

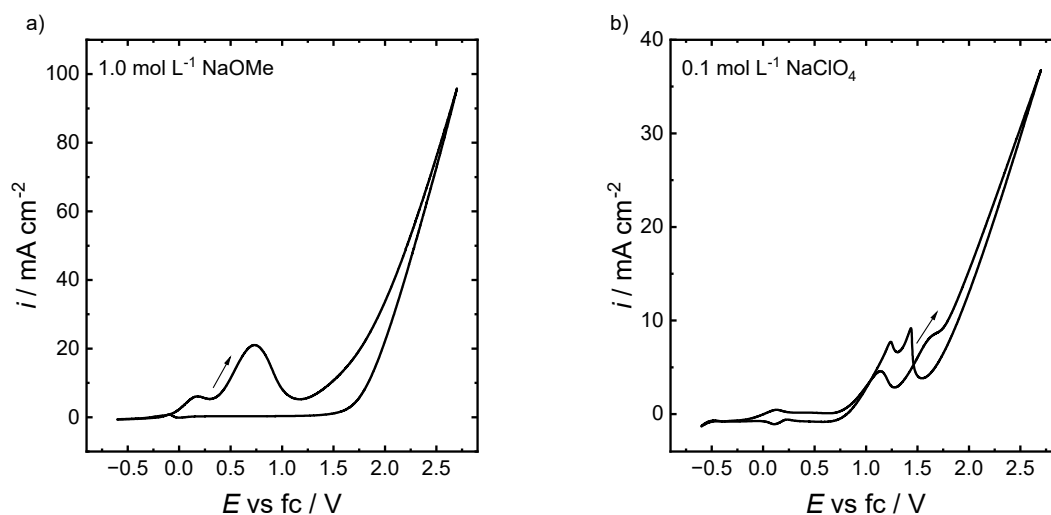


Figure A.2: CVs of a Pt wire at 100 mV s^{-1} in a) $1.0 \text{ mol L}^{-1} \text{ NaOMe}$ and b) $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$.

Table A.11: Formaldehyde and formic acid concentrations determined via HPLC for the H-cell concentrations with varied electrolyte concentrations. These are single point measurements with an HPLC error of 1 %.

$c(\text{NaOMe})$ mol L^{-1}	$c(\text{CH}_2\text{O})$ mg L^{-1}	$c(\text{HCOOH})$ mg L^{-1}
0.1	71	7
0.5	199	13
1.0	176	113

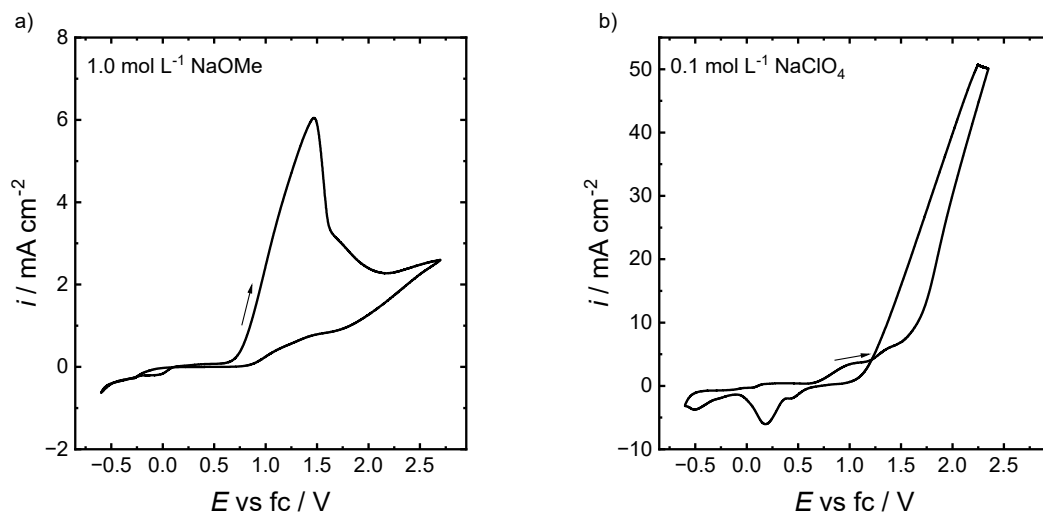


Figure A.3: CVs of a Cu wire at 100 mV s^{-1} in a) $1.0 \text{ mol L}^{-1} \text{ NaOMe}$ and b) $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$.

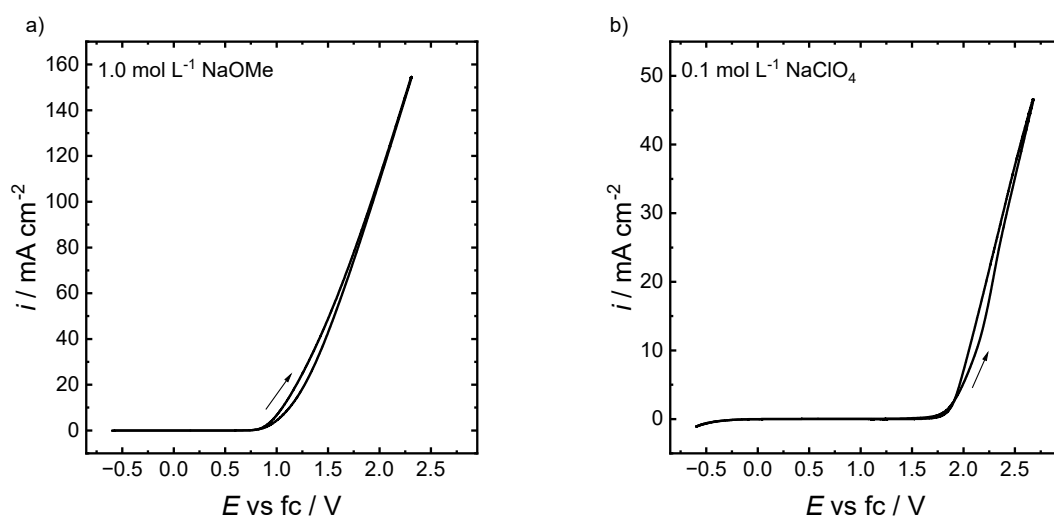


Figure A.4: CVs of a Ni wire at 100 mV s^{-1} in a) $1.0 \text{ mol L}^{-1} \text{ NaOMe}$ and b) $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$.

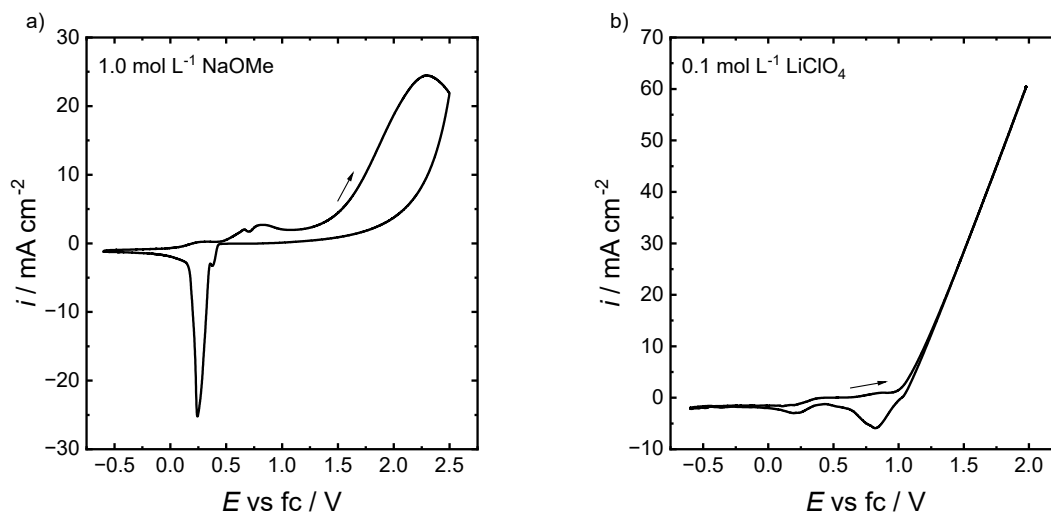


Figure A.5: CVs of an Ag wire at 100 mV s⁻¹ in a) 1.0 mol L⁻¹ NaOMe and b) 0.1 mol L⁻¹ LiClO₄. For LiClO₄, the curve shown is the 5th cycle it was the last complete CV curve obtained due to the instability of the silver wire.

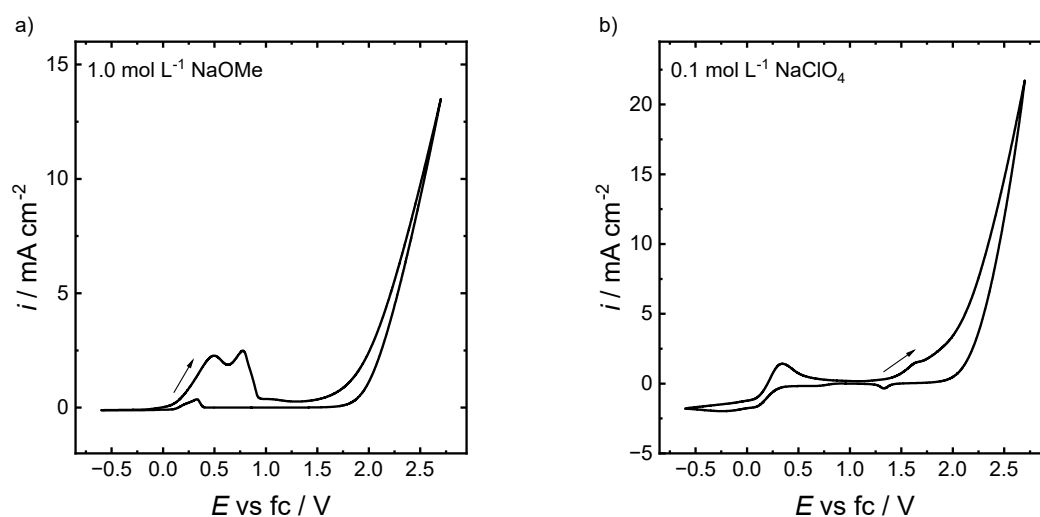


Figure A.6: CVs of a Au wire at 100 mV s⁻¹ in a) 1.0 mol L⁻¹ NaOMe and b) 0.1 mol L⁻¹ NaClO₄.

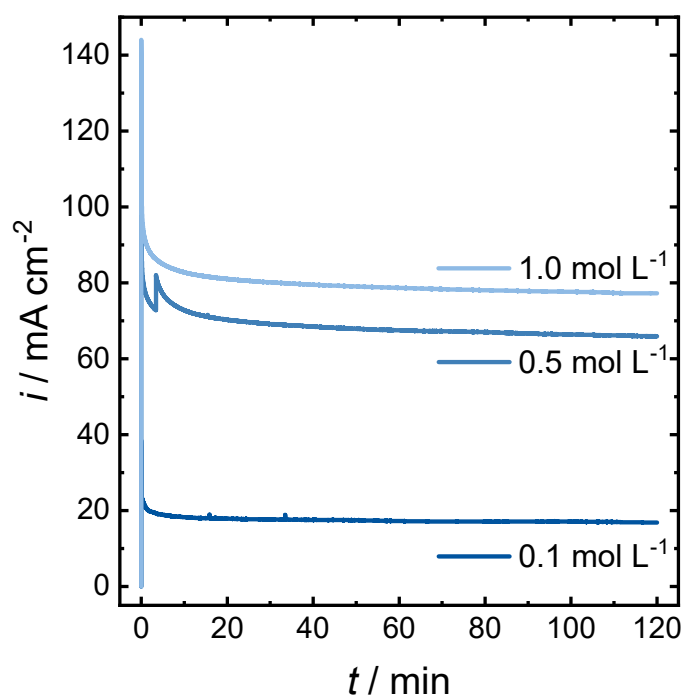


Figure A.7: CAs in different NaOMe concentrations at 2.4 V for 2 h on a platinum working electrode in an H-cell.

A.4 Impact of the scale-up and flow cell parameters on the formaldehyde formation

A.4.1 Variation of flow rates

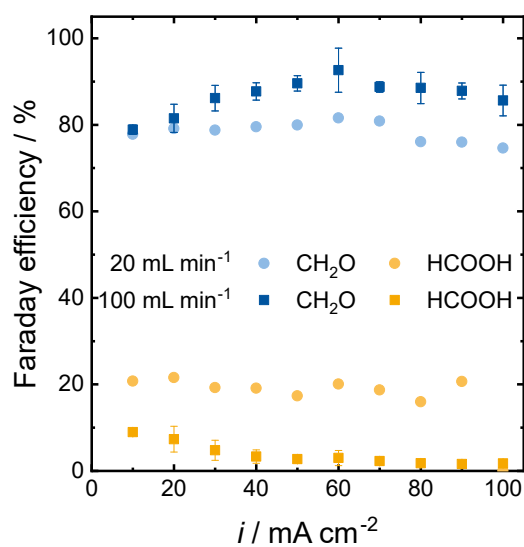


Figure A.8: Faraday efficiencies for formaldehyde (blue) and formic acid (orange) in 0.1 mol L^{-1} NaOMe solutions with flow rates of 20 mL min^{-1} and 100 mL min^{-1} at different current densities.

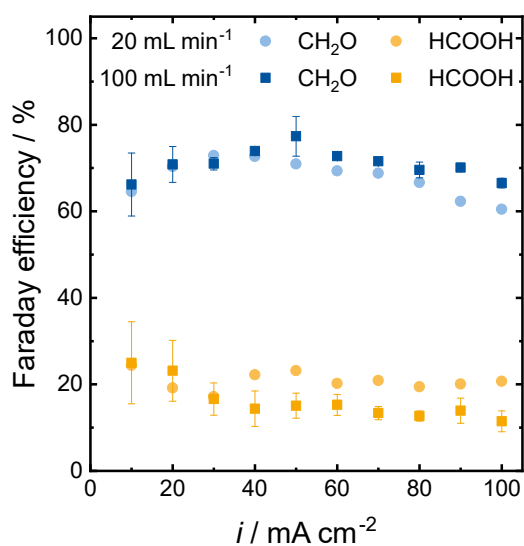


Figure A.9: Faraday efficiencies for formaldehyde (blue) and formic acid (orange) in $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$ solutions with flow rates of 20 mL min^{-1} and 100 mL min^{-1} at different current densities.

A.4.2 Electrode gap

Table A.12: Results of CP experiments of 0.1 mol L^{-1} NaOMe at 10 mA cm^{-2} and 100 mA cm^{-2} with varied electrolyte gaps. Each experiment recirculated 40 mL with a flow rate of 100 mL min^{-1} .

$d_{\text{electrodes}}$ mm	i mA cm^{-2}	E_{cell} V	$c(\text{CH}_2\text{O})$ g L^{-1}	E_s kW h kg^{-1}
4	10	2.37	0.76	5
8	10	3.36	0.77	7
12	10	3.33	0.64	8
4	100	11.30	6.80	25
8	100	17.32	7.65	35
12	100	19.85	6.84	45

Table A.13: Results of CP experiments of 1.0 mol L^{-1} NaOMe at 10 mA cm^{-2} and 100 mA cm^{-2} with varied electrolyte gaps. Each experiment recirculated 40 mL with a flow rate of 100 mL min^{-1} .

$d_{\text{electrodes}}$ mm	i mA cm^{-2}	E_{cell} V	$c(\text{CH}_2\text{O})$ g L^{-1}	E_s kW h kg^{-1}
4	10	2.86	0.55	8
8	10	2.98	0.63	7
12	10	3.09	0.50	10
4	100	5.11	3.89	20
8	100	6.32	3.61	27
12	100	7.38	2.68	43

A.5 Influence of the supporting electrolyte

A.5.1 Electrolyte characterization

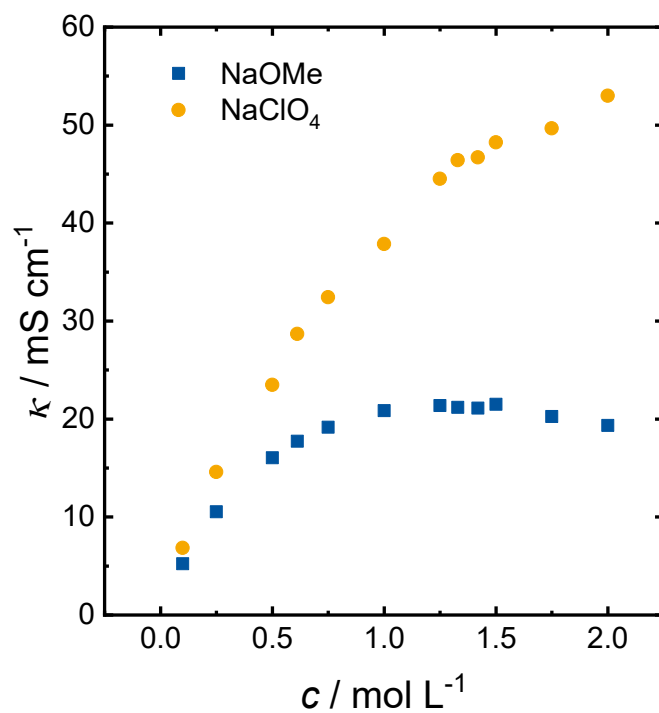


Figure A.10: Electrical conductivity of different concentrations of NaOMe (blue) and NaClO₄ (orange).

A.6 Influence of the formaldehyde concentration

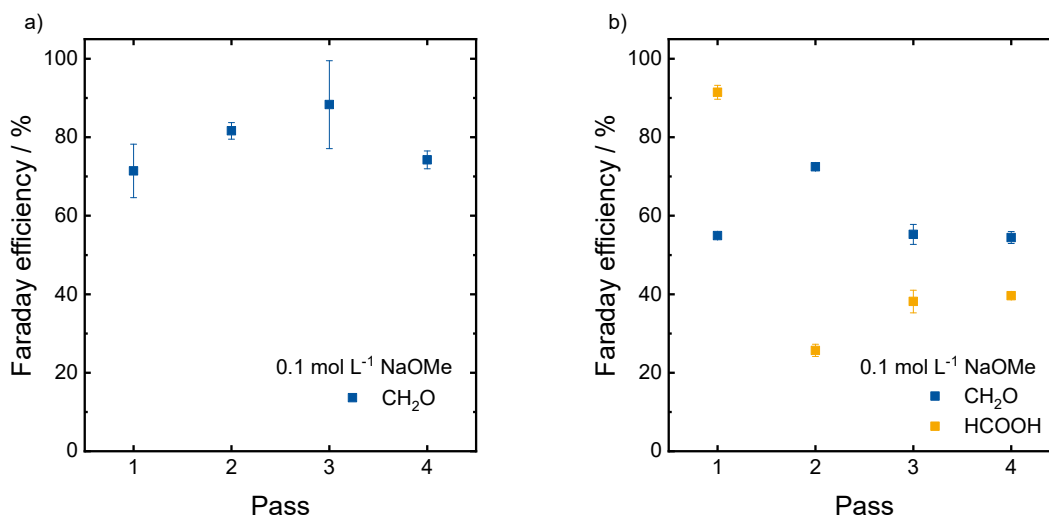


Figure A.11: Faraday efficiency over four passes for a) 0.1 mol L⁻¹ and b) 1.0 mol L⁻¹ NaOMe at 10 mA cm⁻². Each pass was performed on platinum for 30 min at 10 mA cm⁻² with 400 mL electrolyte as a single pass with a flow rate of 10 mL min⁻¹. The electrolyte was then used for the subsequent pass.

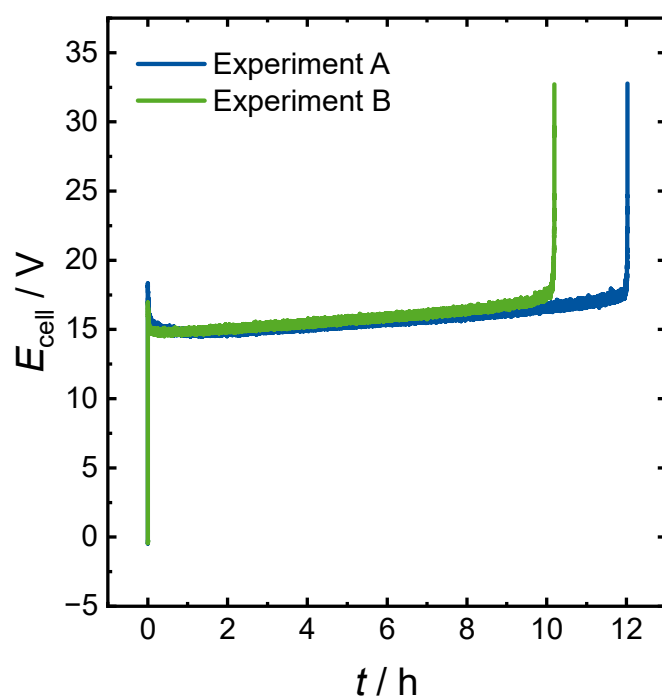


Figure A.12: Cell potentials of the recirculation experiments for 16 h. The measurements were interrupted after 12 h and 10 h, respectively, due to the compliance voltage becoming too large.

A.7 Investigations of the reaction mechanism

A.7.1 Potential influence on the reaction mechanism

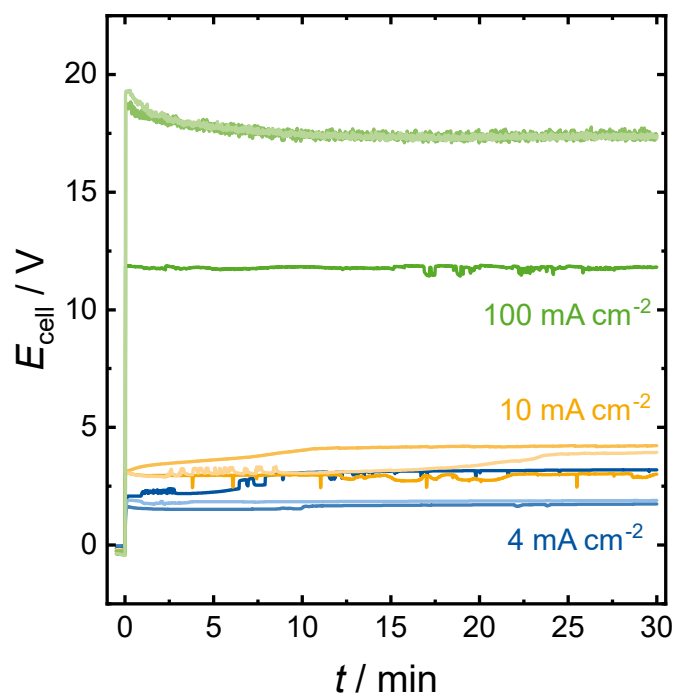


Figure A.13: E_{cell} in 0.1 mol L^{-1} NaOMe at 4 mA cm^{-2} (blue), 10 mA cm^{-2} (orange), 100 mA cm^{-2} (green). The experiments were performed on a platinum foil anode for 30 min with 40 mL electrolyte and a flow rate of 100 mL min^{-1} .

A.7.2 ATR-SEIRA spectroscopy and surface species analysis

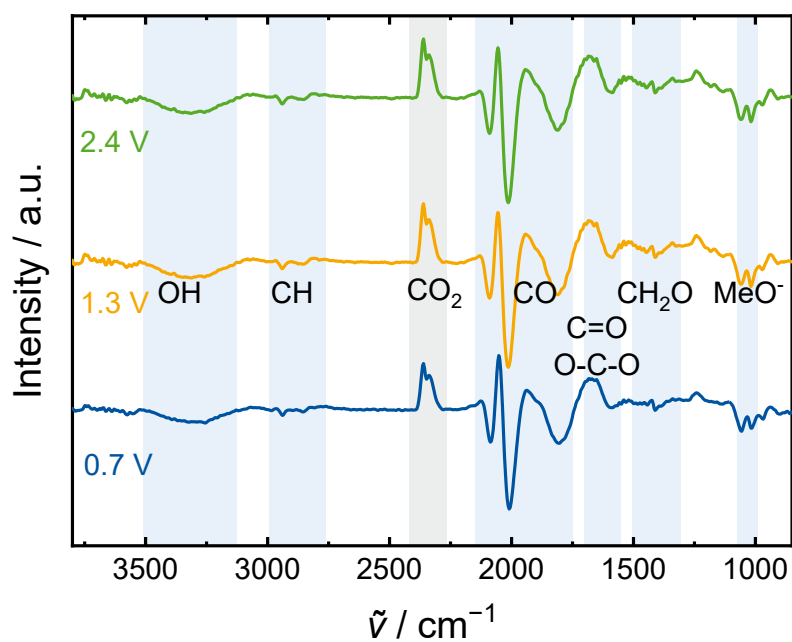


Figure A.14: ATR-SEIRA spectra of 0.1 mol L^{-1} NaOMe in methanol at 0.7 V, 1.3 V, and 2.4 V vs fc recorded on a platinum thin film electrode in the ATR-cell. A Ag-wire was used as a pseudo reference electrode.