# Electrolyte Influence on the Electrochemical Oxidation of Anhydrous Methanol to Dry Formaldehyde

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The electrification of the formaldehyde synthesis is investigated as a sustainable alternative to the current thermal approach. The formation of formaldehyde in anhydrous methanol achieves higher Faraday efficiencies than in aqueous conditions, yet operates at higher cell potentials. The electrolyte is an influential factor, and its role is not yet understood. Here, we report on the electrolyte's effect on the electrochemical formaldehyde synthesis in anhydrous methanol. After an electrolyte screening, four electrolytes were chosen for an in-depth analysis of the supporting electrolyte's ion influence. Among the tested supporting electrolytes, the anion dominates the conductivity and viscosity while larger cations favor the formation of formaldehyde. Understanding the electrolyte properties is crucial for large-scale industrial synthesis.

**Keywords:** Electrification, Electrooxidation, Electrosynthesis, Green chemistry, Water-free electrolysis

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## 1 Introduction

Formaldehyde is a versatile platform chemical that is used for polymers, resins, and glues [1]. The commonly applied synthesis involves the thermally induced oxidation of methanol at elevated temperatures [1, 2]. With the energy transition to renewable electricity, the electrification of industrial processes is required. The electrochemical synthesis of formaldehyde can be carried out via the oxidation of aqueous [3, 4] or non-aqueous methanol [5, 6] or the reduction of $CO_2$ [7]. In our previous work we found that the formaldehyde synthesis based on anhydrous methanol yields Faraday efficiencies (FEs) of up to 90 % at elevated current densities in a scaled-up flow reactor [5]. With anhydrous methanol, higher FEs were achieved while also requiring higher potentials compared to the electrochemical oxidation of aqueous methanol [8]. Thus, the electrolyte influences were investigated in more detail to analyze its impact on the FE and cell potential.

For the electrochemical oxidation of aqueous methanol to formaldehyde it was found that the efficiency and selectivity depend on the acid-base properties of the electrolyte [9], adsorbed surface species [10], mass transport [3], and methanol concentration [3, 4].

The electrochemical oxidation of anhydrous methanol also strongly depends on the electrolyte; yet, its influences are not fully understood. Early investigations found that some supporting electrolytes, such as NaOMe and $NH_4F$, favor the formation of formaldehyde [11, 12], others lead to longer carbon chains [13]. It was also reported that larger halide anions hinder the formaldehyde formation [7, 11]. Chloride-containing electrolytes have the additional challenge of platinum poisoning due to a strong Pt-Cl interaction [14]. Alkalinity, to a certain degree, seems to be required to form formaldehyde [6], whereas a too high alkalinity favors the formation of formic acid [5]. No systematic approach has been reported to investigate the effect of the electrolyte on the oxidation of anhydrous methanol to formaldehyde. Yet, understanding the electrolyte influence is vital to optimize the process parameters and achieve better Faraday and energy efficiencies to scale the electrochemical formaldehyde synthesis to industrial applicability.

Here, the performance of eight electrolytes under comparable measurement conditions is reported, considering also the impact of concentration and current density. Of the

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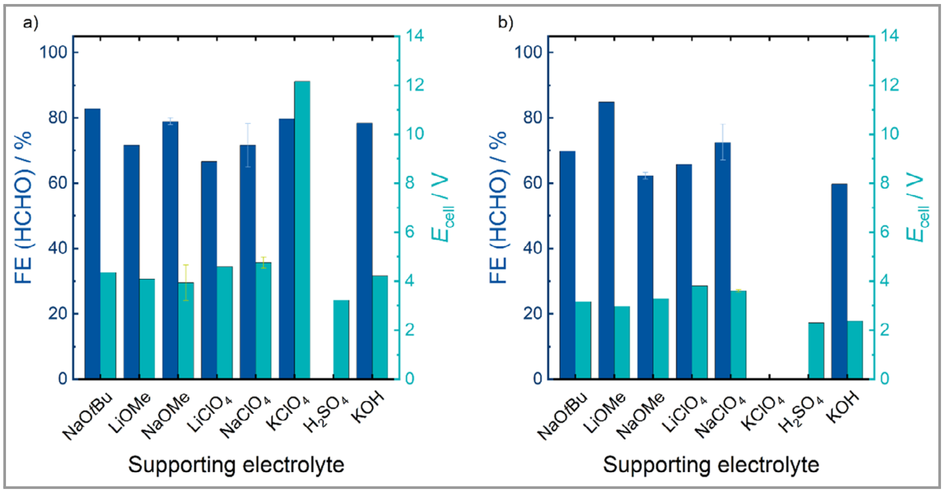

**Figure 1.** FE for formaldehyde (blue) and the corresponding cell potentials (cyan) for different electrolytes with concentrations of a) 0.1 mol $L^{-1}$ and b) 1.0 mol $L^{-1}$ in methanol. The cell potentials are measured at an applied current density of 10 mA $cm^{-2}$.

tested electrolytes, NaOMe, LiOMe, $NaClO_4$, and $LiClO_4$ were characterized in more detail by their acid-base properties, viscosity, and conductivity. This allows a profound understanding of the supporting electrolyte's ion influence as well as of the overall electrolyte properties. It also enables us to correlate the performance of the formaldehyde formation in different electrolytes with their physicochemical properties.

## 2 Results and Discussion

This study investigates the influence of the supporting electrolytes on the oxidation of anhydrous methanol. However, methanol is known to contain small amounts of water. In a previous work we showed that the water content in open H-cell setups varies between 0.1 and 0.2 wt % [5]. An artificial increase of the water concentration in the H-cell indicates that less formaldehyde forms at water contents increase ≥ 5 wt % (Fig. S1 in the Supporting Information SI) possibly due to total methanol oxidation [9]. For this study, the water content of methanol and freshly prepared 0.1 mol $L^{-1}$ NaOMe and 1.0 mol $L^{-1}$ NaOMe were measured via Karl Fischer coulometry. The water content of the freshly prepared solutions for the flow cell experiments was between 0.001 and 0.05 wt % (Tab. S1 in SI). Considering this low water content, its impact on the efficiency of the process was neglected for this study but could possibly be studied in more detail in the future.

### 2.1 Electrolyte Screening

Four different types of electrolytes were selected: methoxide-based electrolytes (NaO*t*Bu, LiOMe, NaOMe), perchlorate electrolytes ($LiClO_4$, $NaClO_4$, $KClO_4$), as well as acidic ($H_2SO_4$), and alkaline (KOH) electrolytes. Please note that NaO*t*Bu is considered as a methoxide electrolyte because it is more basic than methanol and forms *tert*-butanol and NaOMe by methanol deprotonation [15]. The FE for formaldehyde in all electrolytes that provided a stable cell potential is depicted in Fig. 1. Two supporting electrolyte concentrations (0.1 and 1.0 mol $L^{-1}$) in methanol were tested.

At low electrolyte concentrations, all methoxide and perchlorate electrolytes as well as KOH show high FEs to formaldehyde (67 % ($LiClO_4$) to 83 % (NaO*t*Bu)) with similar cell potentials between 3.9 V (NaOMe) and 4.8 V ($NaClO_4$). The cell potential of $KClO_4$ 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 ($c < 0.1$ mol $L^{-1}$). As overall trend for methoxide and perchlorate electrolytes, the FE rises with increasing cation radius (Li < Na < K). In contrast, $H_2SO_4$ 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 $CO_2$ [9, 16]. The KOH electrolyte facilitated an FE of 78 %, which is comparable to the FE of NaOMe at a slightly higher cell potential of 4.2 V.

With increasing electrolyte concentrations (Fig. 1b), the FEs are lower (5–15 percent points (pps)), but also the cell potentials decrease significantly by approx. 25 % compared to the 0.1 mol $L^{-1}$ electrolytes. The exception is LiOMe, which provides an increased FE of 85 %. Based on the single LiOMe measurement, whose FE needs to be verified, the FE correlation with the cation size cannot be confirmed for the methoxide-containing electrolytes (62 % FE for NaOMe vs. 85 % FE 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 slightly lower FEs and a cell potential lower than the methoxide- and perchlorate-based electrolytes.

**Table 1.** Overview of the p$K_a$ values to the corresponding acids of the aqueous supporting electrolytes.

| Supporting electrolyte | Conjugated acid | p$K_a$ [18] |
|---|---|---|
| LiOMe | MeOH | 15.5 |
| NaOMe | MeOH | 15.5 |
| $LiClO_4$ | $HClO_4$ | −1.6 |
| $NaClO_4$ | $HClO_4$ | −1.6 |

Further supporting electrolytes ($CH_3COOH$, $H_3PO_4$, $KH_2PO_4$, $K_2HPO4$, $Na_2SO_4$) were tested, but were not further investigated because of their low conductivity or low solubility in methanol.

### 2.2 Electrolyte Characterization

Out of the tested electrolytes, LiOMe, NaOMe, $LiClO_4$, and $NaClO_4$ were characterized in more detail, as they each differ in either cation or anion to two other salts. This allows to investigate the ion influence of the electrolytes and the electrolyte properties. The acid-base properties are known to be strongly influential on the occurring electrochemical reaction pathway [9, 17]. Furthermore, the viscosity and the conductivity of the electrolytes were measured as they are important process parameters for industrial application.

#### 2.2.1 Acid-Base Properties

The acid-base properties are often described by the p$K_a$ value that represents the acid strength of a substance. The lower the p$K_a$ value, the stronger the acid. The investigated supporting electrolytes are salts of the corresponding acids. Thus, the p$K_a$ values for the acids were taken from literature and are summarized in Tab. 1.

The p$K_a$ scale is defined by an aqueous environment. Yet, p$K_a$ 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 Li < Na < K [19], which matches the hard and soft acids and bases (HSAB) theory [20].

#### 2.2.2 Viscosity

Generally, the viscosity of the electrolyte influences the mass transport. A significant viscosity difference was visually observed for NaOMe electrolyte with increasing concentration. Thus, the viscosity for all four electrolytes was measured. This allows a systematic analysis of the anion's and cation's influence. The determined viscosities are displayed in Fig. 2 at 0.1 mol $L^{-1}$ (blue) and 1.0 mol $L^{-1}$ (green), respectively.

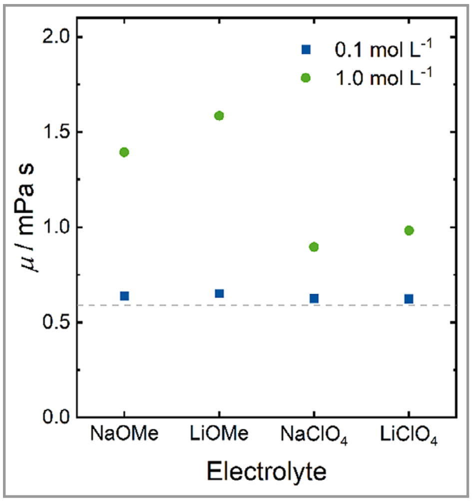

**Figure 2.** Viscosity of NaOMe, LiOMe, $NaClO_4$, $LiClO_4$ at concentrations of 0.1 mol $L^{-1}$ (blue) and 1.0 mol $L^{-1}$ (green). The gray line shows the viscosity of pure methanol.

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 lithium cation. The Coulombic interactions within an electrolyte are also affected by its alkalinity and, thus, by the dissociation of the salt within the solvent, which 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: $NaClO_4$ < $LiClO_4$ < NaOMe < LiOMe.

#### 2.2.3 Conductivity

Varying the supporting electrolyte also influences the conductivity of the electrolyte. To compare the effect of the individual ions of the supporting electrolyte, the conductivity of methanolic LiOMe, NaOMe, $LiClO_4$, and $NaClO_4$ were measured at 0.1 and 1.0 mol $L^{-1}$. The conductivities are depicted in Fig. 3.

For lower concentrated electrolytes ($c$ = 0.1 mol $L^{-1}$), the conductivities of the perchlorate salts (7.3 mS $cm^{-1}$)

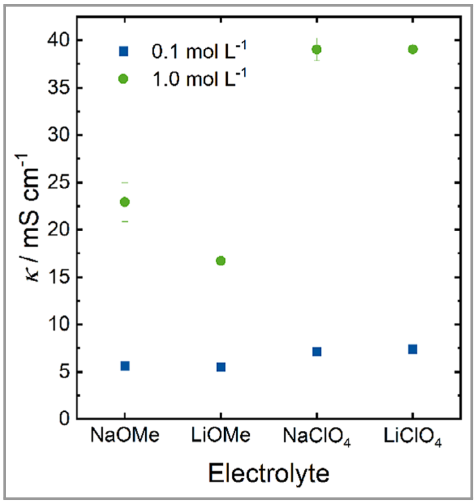

**Figure 3.** Conductivity of NaOMe, LiOMe, $NaClO_4$, $LiClO_4$ at concentrations of 0.1 mol $L^{-1}$ (blue) and 1.0 mol $L^{-1}$ (green) at room temperature.

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 $NaClO_4$) being more conductive than methoxide-containing electrolytes (23.0 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.

In conclusion, the anion also dominates the conductivity behavior. The higher conductivities of the perchlorate electrolytes indicate an increased ion mobility 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 lithium cation.

## 2.3 Comparison of the Electrolyte Performance for the Formaldehyde Formation

The performance of the electrolyte was evaluated by measuring the FE for formaldehyde and calculating the specific energy consumption ($E_s$) for selected electrolytes in a current density range from 10 to 100 mA $cm^{-2}$. An overview of the FEs for formaldehyde for the four electrolytes is given in Fig. 4. The individual graphs for each electrolyte as well as the FE for the liquid by-product formic acid are illustrated in Figs. S2–S5 in the SI.

At 0.1 mol $L^{-1}$ (Fig. 4a), all newly tested electrolytes perform slightly worse than the reference electrolyte NaOMe with FEs between 79–90 %, as also reported earlier [5]. Nevertheless, in all electrolytes, stable FEs of > 60 % are obtained. The use of LiOMe and $NaClO_4$ results in similar FEs while employing $LiClO_4$ produced the lowest FEs. In general, the methoxide electrolytes perform better than the perchlorate ones and the sodium salts perform better than the lithium salts. The reaction performance is, among others, dominated by the electrolyte's 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. The viscosity for all electrolytes is similar to that of pure methanol and no influence can be deduced.

The performance of the supporting electrolytes differs strongly when using 1.0 mol $L^{-1}$ electrolytes (Fig. 4b). Here, $NaClO_4$ yields the highest FEs and it is the only supporting electrolyte whose FEs increased at higher concentration. The obtained FEs for $LiClO_4$ remained constant whereas the ones for the methoxide salts decreased. Furthermore, the FEs measured for $NaClO_4$ stay almost constant across

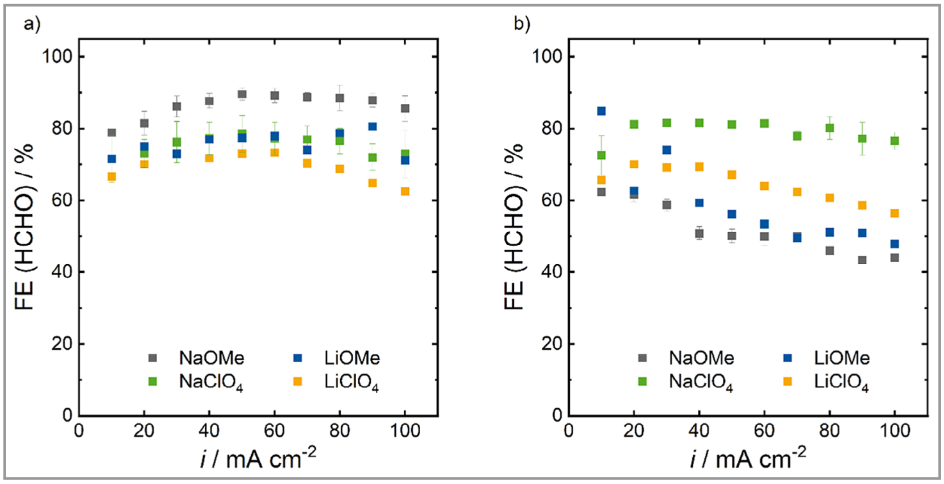

**Figure 4.** Comparison of the FE for formaldehyde in a) 0.1 mol $L^{-1}$ and b) 1.0 mol $L^{-1}$ in different electrolytes as a function of the current density.

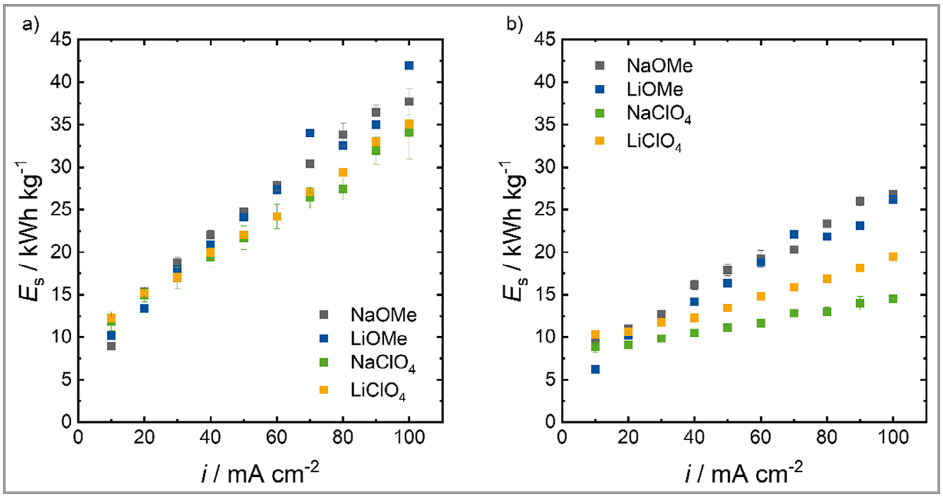

**Figure 5.** Comparison of the specific energy consumption for formaldehyde in a) 0.1 mol L$^{-1}$ and b) 1.0 mol L$^{-1}$ in different electrolytes as a function of the current density.

the current density range. All other supporting electrolytes show a decrease in the FE with increasing current densities. $LiClO_4$ performs better than both methoxide salts while NaOMe provides the lowest FEs to formaldehyde. The methoxide electrolytes now yield significantly lower FEs compared to the perchlorate salts, but also to themselves at 0.1 mol L$^{-1}$. For both methoxide and perchlorate electrolytes, the conductivity and viscosity increase with increasing concentration. However, the alkalinity remains near neutral for the perchlorates but increases significantly for the methoxides. This suggests that too highly alkaline electrolytes disfavor the formation of formaldehyde. Instead, formic acid is produced in increasing amounts, indicating that a different reaction pathway becomes favored.

Looking at the alkalinity of the individual salts, the use of LiOMe results in slightly higher FEs while being less alkaline than NaOMe [19], which implies that the 1.0 mol L$^{-1}$ methoxide electrolytes are too alkaline. 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. This indicates that the perchlorates could benefit from being more alkaline. The viscosity of all electrolytes rises with increasing concentration, though less for the perchlorates. $NaClO_4$ yields the highest FEs while having the lowest viscosity, indicating that a fast mass transport favors formaldehyde formation. For the methoxide electrolytes, NaOMe is less viscous than LiOMe but yields lower FEs. No clear influence of the viscosity on the FE can be deduced. The investigated electrolyte properties cannot explain all the observed trends for the FE, which demonstrates that additional factors of the electrolyte need to be taken into account.

While no correlation between the FE and the viscosity or conductivity could be observed, they clearly influence the cell potential. Generally, a high cell potential equals a high energy consumption, and a high Faraday efficiency equals a low energy consumption. The ratio between the required energy and the FE can be expressed via the specific energy consumption ($E_s$) (Eq. (1)).

$$E_s = \frac{E_{\text{cell}} \cdot z \cdot F}{\text{FE} \cdot \nu_p} \tag{1}$$

The specific energy consumptions for all electrolytes are indicated in Fig. 5.

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$^{-1}$ ($LiClO_4$) at 10 mA cm$^{-2}$ and increases linearly with rising current densities to a range of 34 kWh kg$^{-1}$ ($NaClO_4$) to 42 kWh kg$^{-1}$ (LiOMe). The FE 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 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 (Fig. S5 in the SI), while having a slightly lower viscosity and equal conductivity. As the Na-electrolytes also lead to higher FEs, it compensates for the higher cell potentials and the $E_s$ for both methoxide- and perchlorate-salts overlap, 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 and faster reaction kinetics. Yet, the cell potentials are higher for the Na-electrolytes which indicates that the cation influences more than just the viscosity and the conductivity.

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) and, thus, is lower compared to the diluted electrolytes (Fig. 5b). For the methoxide electrolytes, the $E_s$ appears independent of the cation. Because of its lower conducitivty, LiOMe has higher cell potentials (Fig. S6 in the SI) that are compensated by higher FEs. Both perchlorate salts have identical cell potentials, but the $E_s$ for the $NaClO_4$ electrolyte is lower as higher FEs were achieved. The difference to $LiClO_4$ widens with increasing current densities as the FEs 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 $E_s$.

## 3 Summary and Outlook

In this study, the effect of several alkaline and acidic electrolytes on the electrochemical formaldehyde synthesis in anhydrous methanol was investigated. All supporting electrolytes were tested in two different concentrations (0.1 and 1.0 mol $L^{-1}$). Several alkaline supporting electrolytes facilitated the formaldehyde formation (up to 90 % FE) whereas the highly acidic electrolyte did not produce formaldehyde. Perchlorates were tested as supporting electrolytes in the neutral pH region and also showed good activity for the formaldehyde formation. For methoxide and perchlorate electrolytes, larger cations seem to favor the selectivity to formaldehyde.

The methoxide- and perchlorate-based electrolytes differ in either anion or cation exchange and were investigated further with respect to their viscosity and conductivity and further correlated with their respective acid-base properties. The analysis of the systematic ion variation indicates that the measured electrolyte properties are dominated by the anion. The methoxide-based electrolytes are more alkaline, more viscous, and less conductive than the perchlorate salts with the same cation. Overall, the cation influences the viscosity of both electrolytes and the conductivity of only the methoxide ones.

Different trends for the FE to formaldehyde are observed for these electrolytes at different concentrations. At low concentrations, the FE for the methoxide electrolytes remains constant after an initial increase for NaOMe and constant throughout for LiOMe. At high concentrations, both methoxide electrolytes show the same trend: the FE decreases as more formic acid forms with increasing current densities. The FE for the perchlorate-based electrolytes peaks at medium current densities at low concentrations, followed by a slight decrease. The behavior differs at high electrolyte concentrations as the FE remains constant for $NaClO_4$ while it decreases for $LiClO_4$ at higher current densities. This indicates different reaction mechanisms for both, varying supporting electrolytes and concentrations, which may be caused by a higher alkalinity and/or viscosity. Therefore, it appears that more than just the measured electrolyte properties influence the overall reaction performance, and those will be investigated in the future. Because of the safety concerns of perchlorates, other neutral electrolytes or additives to the methoxide electrolytes should be examined. These results highlight the importance of the proper electrolyte choice and are a first step in understanding the underlying influences.

## Supporting Information

Supporting information for this article can be found under DOI: https://doi.org/10.1002/cite.202400167.

This section includes the experimental procedure as well as additional figures relevant for this research.

The raw data used in this study can be accessed here: DOI: https://zenodo.org/doi/10.5281/zenodo.14535056.

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## Symbols used

| | | |
|---|---|---|
| $E_s$ | [kW $kg^{-1}$] | specific energy consumption |
| $F$ | [C $mol^{-1}$] | Faraday constant |
| $pK_a$ | [–] | negative logarithm of the acid dissociation constant |
| $z$ | [–] | number of electrons |

## Greek letters

| | | |
|---|---|---|
| $k$ | [mS $cm^{-1}$] | electric conductivity |
| $\mu$ | [mPa $s^{-1}$] | viscosity |
| $\nu_p$ | [–] | stoichiometric factor (=1 for the investigated reaction) |

## Sub- and superscripts

| | |
|---|---|
| a | acid |
| cell | electrochemical cell |
| p | product |

## Abbreviations

| | |
|---|---|
| FE | Faraday efficiency |
| HSAB | hard and soft acids and bases |

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