

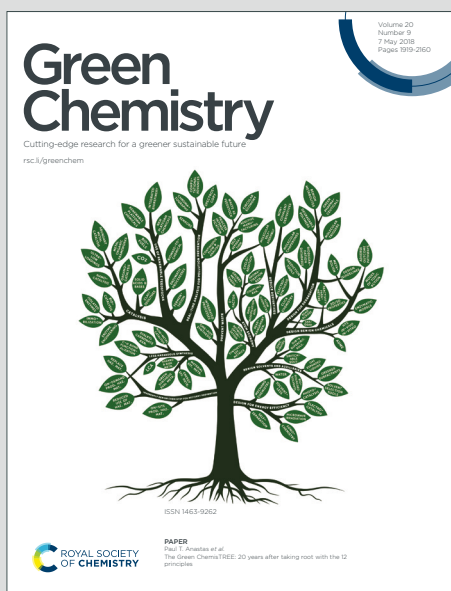
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1. We demonstrate that acetalization of HMF is an effective protection strategy to overcome its instability in strongly alkaline electrolytes. This enables the selective electrochemical oxidation to FFCA, while simultaneously allowing for the production of potentially green hydrogen, thereby generating a valuable intermediate for bio-based polymers.
2. By protecting the aldehyde functionality of HMF during alkaline electrolysis, the carbon balance remains closed, humin formation is suppressed, and high FFCA yields (up to 95%) with Faradaic efficiencies of 90% are achieved. This represents a significant improvement over conventional electrooxidation processes, especially when targeting FFCA as the oxidation product, and therefore highlights a new pathway towards sustainable polymer building blocks.
3. Future advances could include recycling of the protecting group, translation into continuous electrolyzer operation, and targeted optimization of the electrocatalyst to further enhance the oxidation efficiency and assess industrial feasibility.



ARTICLE

Stabilization of 5-HMF in highly alkaline electrolytes through acetalization for the selective electrooxidation to FFCA

Julius Pönhöfer^{a,b}, Moritz Lukas Krebs^{a,*}, and Ferdi Schüth^a

The oxidation products of 5-hydroxymethylfurfural (HMF) and its derivatives are promising monomers for the production of renewable polymers. However, the stability of HMF during electrooxidation in alkaline electrolytes remains challenging due to its degradation into humins, which reduces the carbon yield. To increase HMF stability in alkaline media, a protection strategy based on acetalization of the formyl group is plausible, but it has not yet been evaluated for electrochemical processes. In this study, we successfully transferred this protection strategy to the electrochemical oxidation of HMF in alkaline media. We demonstrate that acetal-protected HMF is highly stable in alkaline electrolytes, even at elevated concentrations and temperatures. Furthermore, we show that the overall selectivity of the electrooxidation shifts from 2,5-furandicarboxylic acid (FDCA) to 5-formyl-2-furancarboxylic acid (FFCA), which is typically not obtained during the alkaline electrooxidation of HMF. High yields (95%) and Faradaic efficiencies (87%) of FFCA were achieved, even at elevated substrate concentrations (250 mM) in 5 M KOH. The carbon balance remained closed throughout the electrooxidation, demonstrating that acetalization of HMF effectively suppresses degradation into humins.

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- 1) We demonstrate that acetalization of HMF is an effective protection strategy to overcome its instability in strongly alkaline electrolytes. This enables the selective electrochemical oxidation to FFCA, while simultaneously allowing for the production of potentially green hydrogen, thereby generating a valuable intermediate for bio-based polymers.
- 2) By protecting the aldehyde functionality of HMF during alkaline electrolysis, the carbon balance remains closed, humin formation is suppressed, and high FFCA yields (up to 95%) with Faradaic efficiencies of 90% are achieved. This represents a significant improvement over conventional electrooxidation processes, especially when targeting FFCA as the oxidation product, and therefore highlights a new pathway towards sustainable polymer building blocks.
- 3) Future advances could include recycling of the protecting group, translation into continuous electrolyzer operation, and targeted optimization of the electrocatalyst to further enhance the oxidation efficiency and assess industrial feasibility.

Introduction

Biomass derived HMF is a promising platform chemical for the transition of the chemical industry from fossil feedstocks to renewable feedstocks^{1,2} which is in accordance with the 12 principles of green chemistry.³ Among its derivatives,

2,5-furandicarboxylic acid (FDCA), an oxidation product of HMF, has received significant attention as it is a monomer for polyethylene furanoate (PEF), a sustainable alternative to fossil based polyethylene terephthalate (PET).⁴⁻⁷ Similarly, 5-formyl-2-furancarboxylic acid (FFCA) represents an attractive intermediate of HMF oxidation, because it can be utilized in the production of 5-aminomethyl-2-furancarboxylic acid (AMFCA) via reductive amination.^{8,9} Recently the polymerization of 5-aminomethyl-2-furancarboxylic acid (AMFCA) to poly(5-aminomethyl-2-furoic acid) (PAMF), a renewable polyamide with comparable thermal properties to commercial polyamides, has been investigated.¹⁰ In addition, AMFCA can be converted to 8-oxa-3-azabicyclo[3.2.1]octan-2-one¹¹ a monomer for tetrahydrofuran based polyamides,^{11,12} or it can be used for the production of bio based nylon 6 (see Scheme 1a).^{13,14} Moreover, building blocks for organic synthesis, such as

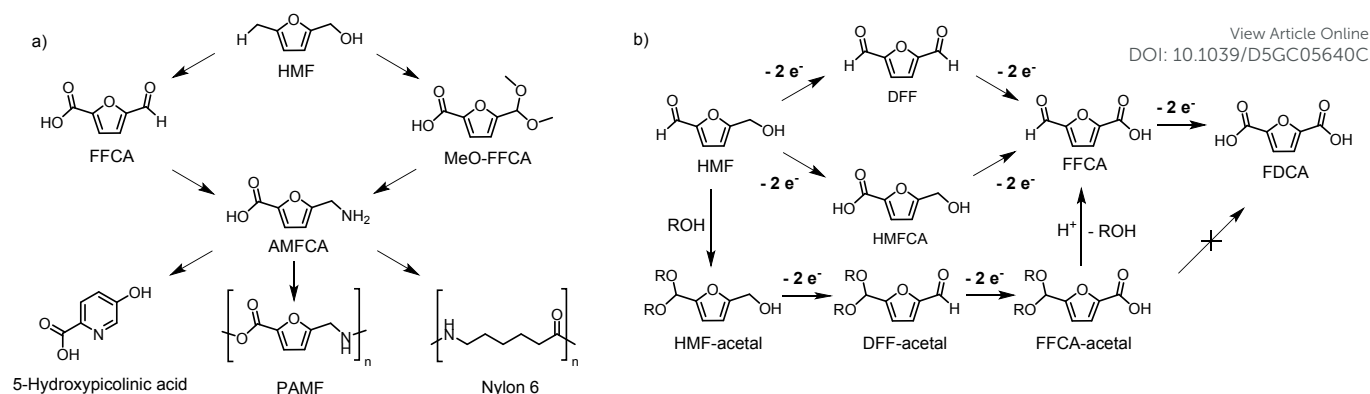
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Scheme 1: a) Oxidation of HMF to FFCA with potential applications and follow up products of FFCA. b) Reaction pathways during the electrooxidation of HMF and HMF acetals for the selective synthesis of FFCA. Further oxidation of the FFCA acetal to FDCA is prevented by the protecting group. Deprotection of the FFCA acetal yields FFCA.

5-hydroxypicolinic acid, can be obtained by further conversion of AMFCA,¹⁵ highlighting FFCA as an increasingly important derivative of HMF.

To oxidize HMF to either FFCA or FDCA, electrochemical oxidation of HMF (Scheme 1b) can be utilized as an alternative to noble metal catalysed thermal oxidation, with the benefit of operating at ambient temperature and pressure.¹⁶ In addition, integrating the oxidation of HMF with a suitable cathode reaction, like the hydrogen evolution reaction (HER), would allow for the simultaneous production of value-added products on both the anode and cathode.¹⁷ This approach is particularly attractive, as coupling the HER with anodic electrooxidation of HMF lowers the required voltage for hydrogen production compared to conventional water splitting, owing to the lower equilibrium potential of HMF oxidation relative to the oxygen evolution reaction (OER), while simultaneously preventing the formation of hazardous hydrogen–oxygen mixtures.¹⁸

The electrooxidation of HMF (HMFOR) occurs via consecutive two electron oxidations of the two functional groups. (Scheme 1b). Depending on which functional group in HMF is first oxidized, two reaction pathways are possible. The oxidation of the formyl group would yield 5-hydroxymethyl-furancarboxylic acid (HMFCFA) as an intermediate, while the oxidation of the hydroxyl group in HMF would yield 2,5-diformylfuran (DFF) as an intermediate. Subsequent oxidation of both intermediates yields FFCA. The specific reaction pathway is depending on the pH. In acidic or close to neutral pH, DFF is predominant as intermediate, while the HMFCFA pathway is dominant at more elevated pH.¹⁹ In addition, the electrochemical oxidation typically does not stop at FFCA, but will eventually result in further oxidation to FDCA. Especially under highly alkaline conditions, typically preferred due to significantly enhanced reaction kinetics, only traces of FFCA are obtained, which makes selective HMF electrooxidation to FFCA challenging under those reaction conditions.^{20–22}

In addition, implementation of the electrochemical HMF oxidation itself is significantly hampered by the instability of HMF in alkaline electrolytes. HMF tends to rapidly degrade into polymeric species known as humins.²³ These species are known to be not accessible for further oxidation and therefore significantly reduce the carbon yield of a process.^{24, 25} To solve

this issue, ongoing research focuses on the electrochemical oxidation of HMF in more neutral or acidic conditions. However, this is often associated with significantly reduced oxidation kinetics, elevated anodic potentials and/or reduced selectivity for FDCA formation.^{26–28} As an alternative approach, stabilization of the HMF molecule or its derivatives could enable to perform the electrooxidation under highly alkaline conditions without HMF degradation and other process limitations. As reported by our group, the degradation of HMF can be prevented by the intentional conversion of HMF into HMFCFA and DHMF via the Cannizzaro reaction. The two Cannizzaro products are stable against degradation into humins and can be easily oxidized electrochemically to FDCA, even when utilizing highly alkaline conditions and elevated HMF concentrations.²⁹ Alternatively, Kim et al explored the use of protecting groups for the stabilization of HMF during the thermal oxidation of HMF.³⁰ The formyl group of HMF was protected with an acetal group in order to suppress the formation of humins. Among the three tested alcohols, the acetal with 1,3-propanediol (PDO) showed the highest stability and the protecting group could be recovered to 80%.³⁰ The protection strategy was further expanded to the oxidative esterification of HMF with methanol, ethylene glycol and PDO as protection group.^{31–33} Although more laborious, this approach offers the advantage of protecting the aldehyde group from further oxidation, potentially enabling shifts in product selectivity, eventually also increasing FFCA yields in the alkaline HMFOR. To date, however, the use of protecting groups in the electrooxidation of fine and commodity chemicals is scarcely reported. A notable example is the electrooxidation of solketal, an acetal-protected form of glycerol, first reported by Cychy et al.³³, whose electrooxidation shifts selectivity from formic acid to the more valuable glyceric acid while suppressing C–C bond cleavage.^{34–36} Yet similar strategies have not been tested for the electrooxidation of HMF.

Inspired by the works of Kim et al. and Cychy et al., we demonstrate for the first time the feasibility of HMF electrooxidation using acetal-protected HMF equivalents. Aldehyde protection significantly enhances stability, even at elevated temperatures and under high KOH and substrate concentrations, achieving yields beyond 80% irrespective of



reaction conditions. Furthermore, the acetal protecting group remains stable under highly alkaline conditions and applied anodic potentials, thereby maintaining aldehyde protection. As a result, high product selectivity for FFCA is achieved, which is otherwise not attainable in the direct electrooxidation of HMF under these reaction conditions.

Results and discussion

Three different HMF acetals were synthesised by following a typical organic synthesis protocol (see ESI for further information: HMF acetal synthesis). The acetal with HMF and 1,3-propanediol (PDO-HMF) and the acetal with ethylene glycol (EG-HMF) were chosen as models for a cyclic acetal while the one with methanol and HMF (MeO-HMF) was chosen as model for an acyclic acetal.

The stability of the acetals was tested in a typical electrolyte solution (1 M KOH), providing initial insights into the suitability of the protection strategy in alkaline electrolytes. All HMF acetals demonstrate no degradation over 30 hours in 1 M KOH at room temperature (Figure 1a). Meanwhile, HMF degrades readily from 100% to 14% over the same period. The HMF acetals show high stability even at 80 °C, while HMF is already degraded after the first measurement after 2 hours (Figure 1b). No significant differences have been observed between the three acetals in contrast to thermal catalysis, where PDO-HMF was the most stable acetal.³⁰ The PDO-HMF and MeO-HMF are even stable at 80 °C in 5 M KOH over 40 h (Figure S1), showing that the HMF acetals might be suitable for industrial conditions. Overall, the HMF acetals seem to be highly stable in alkaline solutions even after extended storage time and at elevated temperature, making them suitable for the electrooxidation of HMF in alkaline media.

The electrochemical measurements of the HMF acetals were conducted using a three-electrode setup in a batch H-cell. The anode and cathode chamber are separated by a FM-FKL-PK-130 cation exchange membrane. A high performance NiFe foam electrode (1cm x 1cm), developed in our group,³⁷ was used as working electrode. A platinum coil served as counter electrode, and a Hg/HgO electrode with 1 M KOH as inner electrolyte was used as reference electrode. For more details on the experimental setup see the ESI. LSV measurements of protected and unprotected HMF (Figure 2a) reveal that the current response of the system is comparable, and no significant difference can be observed between the three HMF acetals. It appears therefore that the modification of the formyl group via acetalization has no significant influence on the current response of the system in the LSV measurements (Figure 2a). Like HMF, the electrooxidation of the HMF acetals seems to occur in the potential region, where the oxidation of Ni(OH)₂ to NiOOH would be expected. The NiOOH species or other high valent Ni species act as chemical oxidant for the oxidation of the HMF and are regenerated by the applied oxidative potential.³⁸ In the presence of an organic substrate, the current response of the system is thus shifted to a lower potential compared to the OER and transitions seamlessly into the OER at higher potentials (at higher potentials bubble formation is visible at the anode).

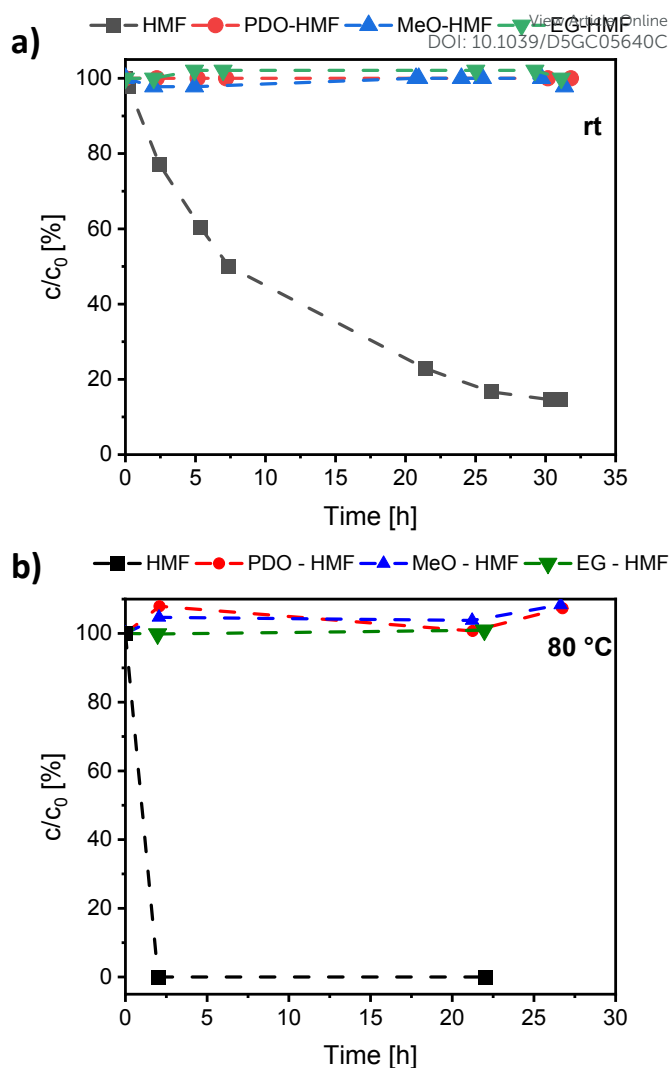


Figure 1: Stability of the HMF acetals (50 mM) in 1 M KOH at a) room temperature b) 80 °C. The stability was followed by qNMR and the initial measured concentration was taken as starting concentration.

To test the product formation in the oxidation of the different organic substrates and current efficiency of the system, the electrooxidation of the HMF acetals was performed at various potentials until a charge equivalent to the complete conversion of the HMF acetal to FFCA (115 C) was transferred. The electrolyte was analysed and the organic molecules quantified by HPLC before and after electrooxidation. Each electrooxidation was performed three times, except for the lowest potential at 1.4 V vs. RHE. The HMF acetals were deprotected on the acidic resin in the HPLC column, thus only unprotected products and starting materials are visible in the HPLC analysis. It is therefore not possible to distinguish between protected and unprotected substrates and products via HPLC. Consequently, it will only be referred to the unprotected compounds in the following discussion. The yields for FFCA are above 83% with a FE above 82% across all applied potentials for the PDO protected acetal (Figure 2b). The selectivity of the reaction is shifted from FDCA as major product in classical HMF electrooxidation under similar



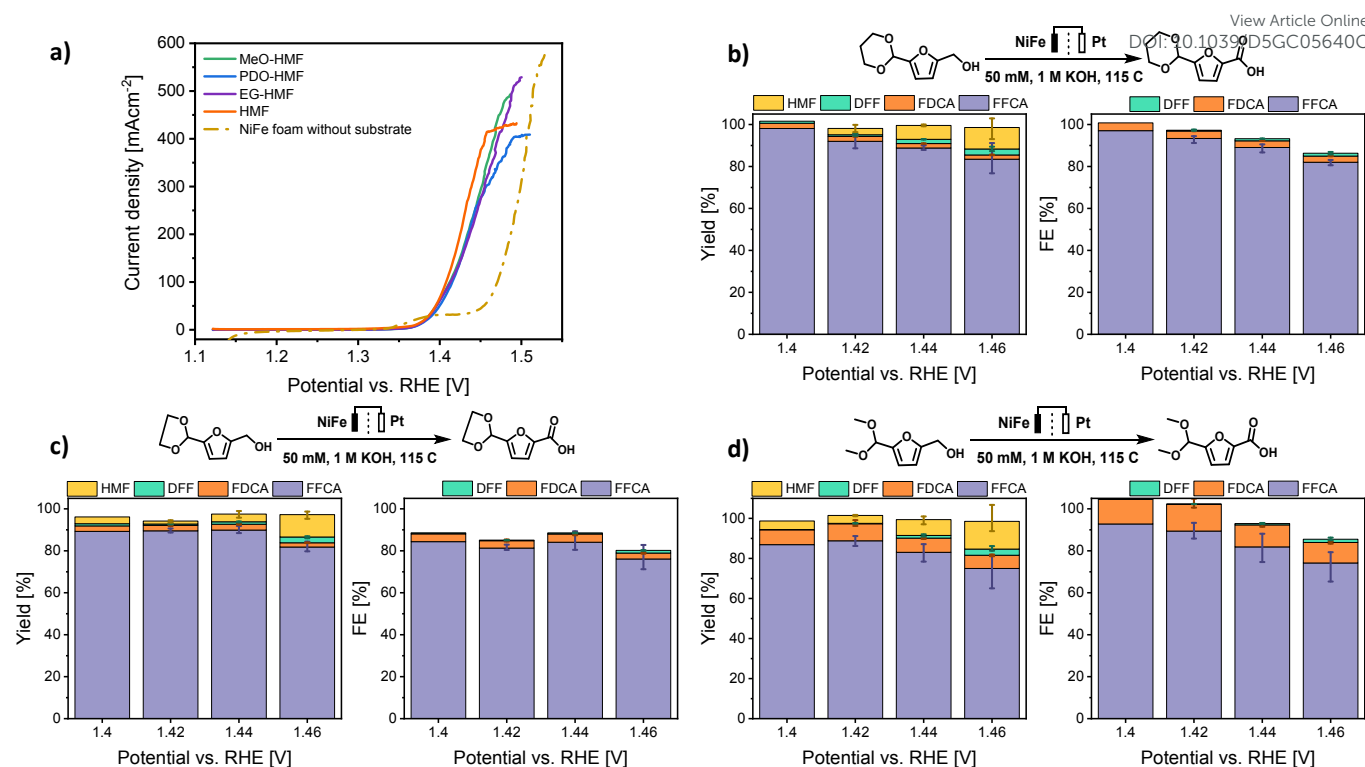


Figure 2: A iron modified nickel foam was used for all measurements. a) LSV of the HMF acetals (50 mM) in 1 M KOH with full iR compensation and a scan rate of 5 mV/s. b) Yields and FE for the electrooxidation of PDO-HMF at constant potential transferring a charge equivalent to full conversion c) for the EG-HMF, d) for the MeO-HMF

conditions (Table S 1) to FFCA as major product due to the protection of HMF with PDO. The yield and FE for FFCA decrease with increasing potential from 98% and 97% at 1.4 V to 83% and 82% at 1.46 V vs. RHE, respectively. This is most likely due to the increasing contribution of the OER as a competing side reaction at higher applied potentials. Since the OER is also consuming transferred charge, the reaction is not able to run until full conversion due to the fixed amount of charge transferred, which also explains the increased concentration of the educt and DFF (reaction intermediate) observed in the HPLC measurements. At 1.40 V vs. RHE no educt can be observed after performing the chronoamperometry. The overall carbon balance remains closed (>98%) across all potentials, indicating the high stability of PDO-HMF under electrooxidative conditions. FDCA can be observed in small yields (around 2%) across all applied potential. The yields for FDCA may be attributed to residues of unprotected HMF from the synthesis of the HMF acetals, since unprotected HMF is typically fully oxidized to FDCA under the applied conditions using the Fe-modified Ni anode.³⁷

In comparison to PDO-HMF, EG-HMF shows no distinct trend across the applied potentials (Figure 2c), with FFCA yields consistently above 82%. The Faradaic efficiency likewise exhibits no clear dependence on potential and remains above 76%. The reduced yields and Faradaic efficiencies, compared to PDO-HMF oxidation, may be influenced by residual ethylene glycol (EG) from the synthesis; however, no oxidation products of EG were detected by HPLC. It should nevertheless be considered that EG may undergo direct oxidation to CO₂, which was not quantified in this study. Similar to PDO-HMF, small

amounts of FDCA (~2.5%) were detected, most likely originating from residual unprotected HMF remaining from the substrate synthesis. Overall, these findings suggest that the protection of HMF with EG is feasible, although further optimization will be required.

Compared to PDO-HMF and EG-HMF, MeO-HMF is a HMF molecule protected by an acyclic acetal group. Nonetheless, it shows a similar trend for the electrooxidation at constant potential with decreasing yield and FE with increasing applied potential (Figure 2d), most likely due to the contribution of the OER. The FFCA yield drops from 87% at 1.4 V to 75% at 1.46 V vs. RHE and the FE for FFCA from 93% to 74%. Similar to PDO-HMF higher concentrations for the starting material and the intermediate DFF are observed at higher potential after passing a fixed amount of charge. The FDCA yield is higher for MeO-HMF, since higher residues of unprotected HMF are present in the educt (Figure S2). The overall carbon balance is closed (>96%) across all applied potentials demonstrating the high stability of MeO-HMF. It should be noted that the presence of the methyl ether as residue from the synthesis decreases the overall activity of the reaction (for a detailed discussion see Chapter 6 in ESI). The substrate should be therefore tested for residues of the methyl ether prior to the electrooxidation and the synthesis needs to be adapted in order to reduce residues of the methyl ether.

Over all the selectivity of the reaction was shifted from FDCA to FFCA due to the protection of HMF with the acetal for all investigated acetals. Under similar conditions, but without protection, HMF is fully oxidized to FDCA (Table S 1), and no FFCA could be detected. To the best of our knowledge, the yield



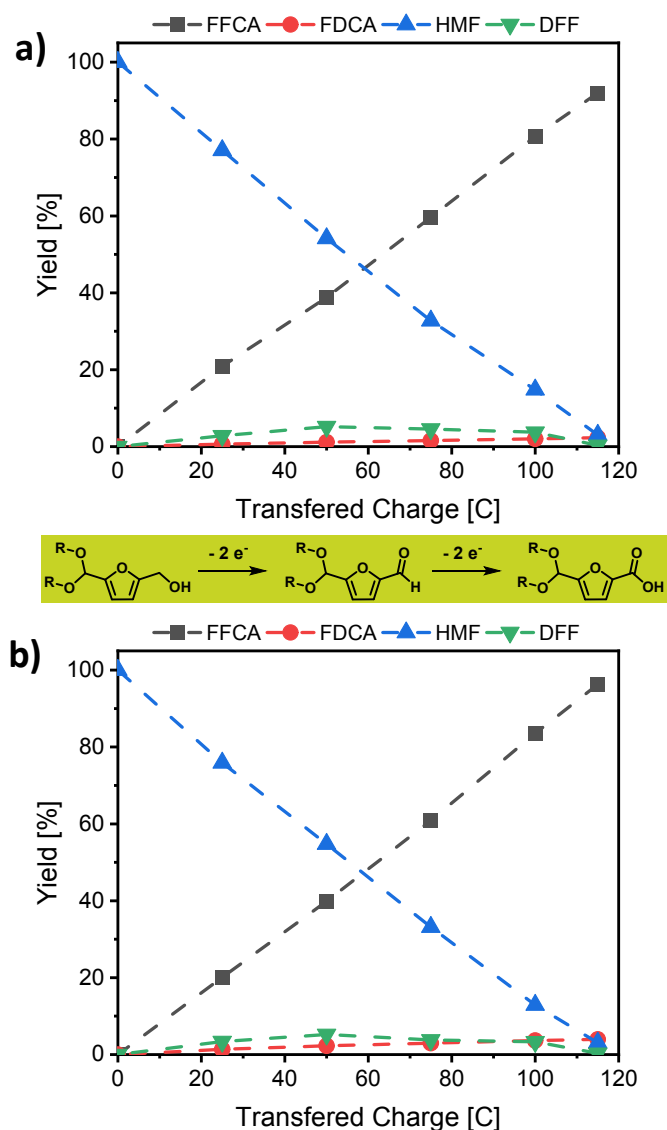


Figure 3: Electrooxidation of the PDO-HMF a) and the MeO-HMF b) followed by charge in 1 M KOH solution using 50 mM of the respective acetal and an Fe modified nickel foam (1 x 1 cm) at 1.42 V.

and selectivity for FFCA is among the highest reported so far in the literature (Table S2). Most other systems use a lower pH or near neutral pH to obtain FFCA as major product.^{20-22, 39} Furthermore, the catalyst needs to be adapted in order to obtain FFCA. With the protection of HMF it is possible to use already developed catalysts for the electrooxidation of HMF. A modification of the catalyst is therefore not necessary, and the HMF acetals could be used as drop in solution in an already existing alkaline electrolyzer. Also, the electrooxidation of the HMF acetals could be performed at lower potentials compared to the direct oxidation of HMF to FFCA reported in literature (Table S2).

During the electrooxidation of HMF, two reaction pathways are possible. The first reaction pathway proceeds via the intermediate DFF and the other one via HMFCa depending on the pH (see Scheme 1b).¹⁸ In contrast to the direct

electrooxidation of HMF, only one reaction pathway should be possible for the electrooxidation of the HMF acetals. The formyl group of HMF is protected by the acetal against further oxidation to the carboxylic acid. Since the reaction pathway via HMFCa requires first the oxidation of the formyl group this reaction pathway is suppressed by the protection and only DFF should be observed after deprotection during HPLC analysis. This is corroborated with charge resolved measurements performed for the electrooxidation of the HMF acetals (Figure 3), which show only DFF as intermediate. In contrast to traditional HMF electrooxidation in alkaline media, no HMFCa could be observed. The reaction proceeds therefore through the DFF pathway, where HMF is first oxidized to DFF and then to FFCA. The relatively low accumulation of DFF might indicate that the first oxidation step from the HMF acetal to the DFF acetal is rate-limiting. Both MeO-HMF and PDO-HMF show similar reaction pathways and behaviour in the charge resolved measurements (Figure 3).

For industrial processes, it is often desirable to increase the electrolyte concentration in order to decrease the solution resistance and with it the overall voltage of the electrolyser.

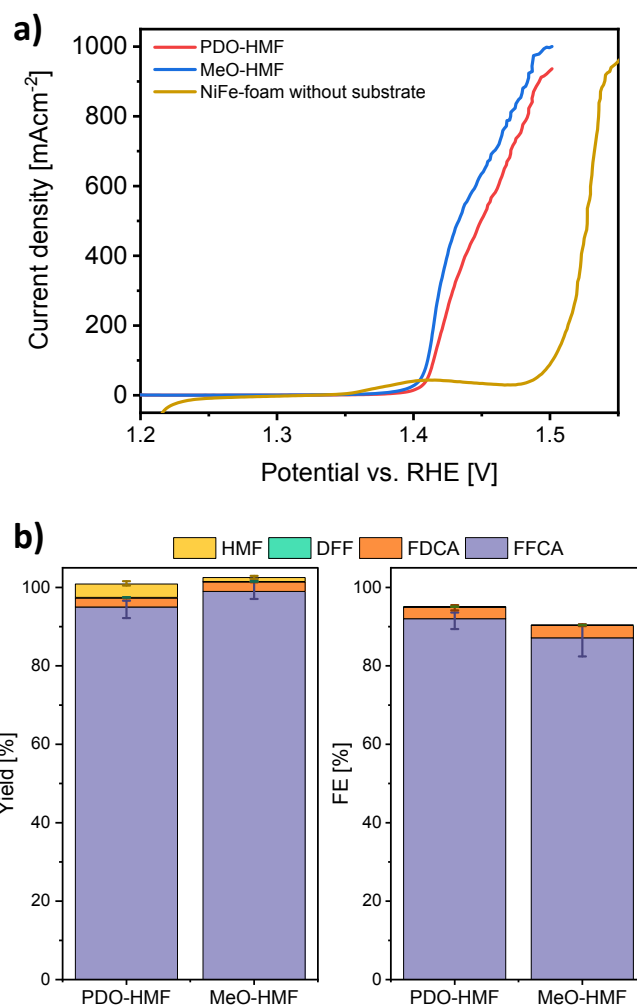


Figure 4: a) LSV of the PDO-HMF (250 mM) and MeO-HMF (250 mM) with a scan rate of 5 mV/s and full iR compensation in 5 M KOH. b) Yields and FE for the electrooxidation of PDO-HMF (250 mM) and MeO-HMF (250 mM) at constant potential in 5 M KOH.

Therefore, the electrolyte and substrate concentrations were increased by a factor of five to 5 M KOH and 250 mM of the HMF acetal to investigate the stability of the HMF acetals under conditions closer to a possible industrial application. The LSVs of PDO-HMF and MeO-HMF at elevated concentrations show a similar current response of the system (Figure 4a), indicating that there might be no difference between an acyclic and cyclic acetal even at elevated concentrations. Similar to previous experiments the electrooxidation appears to occur in the range of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox couple, and the current response is shifted compared to the OER without the HMF acetals. The electrooxidation of the HMF acetals at a constant potential gives high yields for FFCA with 95% for PDO-HMF and 99% for MeO-HMF (Figure 4b). This is the first time that the selective electrooxidation of HMF to FFCA is reported in 5 M KOH. The electrooxidation of unprotected HMF under similar conditions gives FDCA as main product (Table S1, the relatively good yield and FE in spite of the conditions favouring humin formation are due to the stabilization of HMF via the Cannizzaro reaction²⁹). Protection of HMF increases the selectivity for FFCA from <1% to 94% (Table S1). The FE is 92% for PDO-HMF and 87% for MeO-HMF. The closed carbon balance (>99%) as well as the high yields and FE demonstrate the high stability of the HMF acetals even under highly demanding conditions. No significant differences were observed between the cyclic (PDO-HMF) and the acyclic (MeO-HMF) acetal. The carbon balance of unprotected HMF, on the other hand, decreases to 85% utilizing the identical reaction conditions. Yet even more significant carbon losses are expected when the residence time in the alkaline electrolyte is increased further.²⁹

Conclusions

The protection strategy for HMF via acetalization has successfully been transferred from the thermal oxidation of HMF to the electrooxidation of HMF. Three different HMF acetals (PDO-HMF, EG-HMF, MeO-HMF) were investigated for the electrooxidation of HMF in alkaline media. All three HMF acetals demonstrate a high stability in alkaline media, even after 30 hours at ambient temperature or at 80 °C. The protection of the formyl group of HMF shifted the selectivity from FDCA to FFCA, a valuable intermediate. FFCA could be obtained with high yields and FE across all three acetals and applied potentials. The yields and FE remained high even under more demanding conditions, using 5 M KOH and elevated substrate concentrations (250 mM). The carbon balance remained closed during the electrooxidation, demonstrating that the degradation into humins is successfully suppressed. Throughout the study, no significant differences were observed for the current response in the LSV or for yields and FE between the cyclic PDO-HMF and the acyclic MeO-HMF, yet oxidation of the EG-HMF requires additional optimization. To the best of our knowledge, this protection strategy achieved the highest reported yields and selectivity's for FFCA in the literature so far and we were able to demonstrate the production of FFCA as major product in 5 M KOH. Overall, HMF could be successfully

stabilized even in highly alkaline media through the protection strategy and might be used as drop in solution for already existing alkaline electrolyzers. Future research should assess the recoverability of the protecting group in order to develop a comprehensive understanding of the electrooxidation of HMF acetals as an integrated industrial process following the principles of green chemistry. A recycling rate of 80% for PDO³⁰ has been achieved in thermal catalysis with a recycling rate of >91%³¹ in the oxidative esterification of HMF in a two step process. It is conceivable that analogous ratios could be attained for the electrochemical pathway, as no oxidation products of the protecting groups were detected in HPLC.

Author contributions

Julius Ponhöfer: investigation, writing – original draft. Moritz Lukas Krebs: writing – review & editing, supervision. Ferdi Schüth: supervision, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information.

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Data availability statements

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The data supporting this article have been included as part of the Supplementary Information.

