

Integrated Biphasic Electrochemical Oxidation of HMF to FDCA

Tobias Harhues,^{†,‡} Maria Padligur,^{†,‡} Franziska Bertram,[¶] Daniel Roth,[¶] John Linkhorst,[†] Andreas Jupke,[¶] Matthias Wessling,^{†,§} and Robert Keller^{*,†}

[†]*RWTH Aachen University, Chemical Process Engineering, Forckenbeckstrasse 51, 52074
Aachen, Germany*

[‡]*These authors have contributed equally to this work*

[¶]*RWTH Aachen University, Fluid Process Engineering, Forckenbeckstrasse 51, 52074
Aachen, Germany*

[§]*DWI-Leibniz - Institute for Interactive Materials, Forckenbeckstrasse 50, 52074 Aachen,
Germany*

E-mail: manuscripts.cvt@avt.rwth-aachen.de

Abstract

Production of bio-based platform chemicals and polymers via electrochemical routes enables the direct utilization of electrical energy from renewable sources. To date, the integration of electrochemical conversions in process chains remains largely unexplored and the reactions are often studied using synthetic solutions. This work demonstrates the biphasic electro-oxidation of hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) and couples the electrochemical oxidation with the biphasic dehydration of fructose to HMF. The integrated approach eradicates the intermediate HMF purification, as the HMF-rich organic product phase is fed directly into the electrochemical flow-cell reactor. Here, HMF is extracted into the aqueous phase and oxidized to FDCA on a $\text{Ni}(\text{OH})_2/\text{NiOOH}$ catalyst in 0.1 M KOH solution at pH 13. The FDCA then remains in the aqueous phase, enabling direct recirculation of the HMF-containing organic phase. We demonstrate a FDCA yield of close to 80% with a feed from HMF synthesis. Further, we analyze the influence of the phase ratio (V_{Organic} to V_{Aqueous}) and current density for biphasic electrochemical oxidation. By adjusting the gap width, we were able to decrease the average cell voltage from 7 down to 3 V at a current density of 30 mA cm^{-2} . This work presents a promising integrated process for the synthesis of green platform chemicals and provides insight into biphasic solutions in electrochemical conversions.

Keywords

electrochemical process integration, green electrochemistry, electrochemical biomass upgrading, FDCA synthesis

Introduction

Production of polymers accounts for a significant amount of CO₂ emissions, and the production is expected to increase from 380 million metric tons (Mt) in 2015 to approximately 1100 Mt per year by 2050.^{1,2} Sustainable carbon sources like biomass can decrease the environmental impact significantly when sustainable processes are employed.²⁻⁴ 2,5-furandicarboxylic acid (FDCA) is a promising biobased platform chemical and monomer for the chemical industry.⁵ It can be polymerized to different polyesters, polyamides or other polymers,⁶⁻⁸ with polyethylenefuronat (PEF) as the most prominent example.⁹

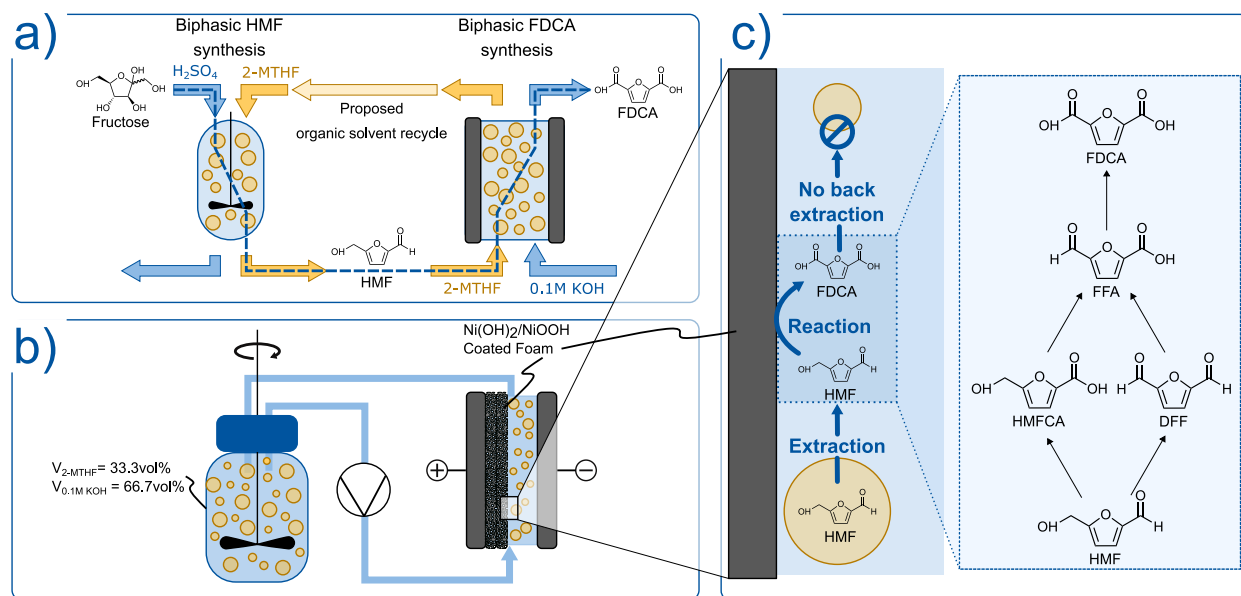
FDCA can be synthesized from C6-sugars, mainly fructose, via different routes, for example via 5-(hydroxymethyl)furfural (HMF).¹⁰ To synthesize HMF, fructose is dehydrated with an acid-catalyzed reaction in aqueous environment. However, HMF is highly reactive and its stability is the main limiting factor of the HMF yield during fructose dehydration.¹¹ The *in-situ* extraction of HMF into an organic phase stabilizes the product and increases the HMF yield.¹¹⁻¹³

Different routes exist to subsequently oxidize HMF to FDCA, for example chemo-catalytic and electrochemical routes.^{14,15} Chemo-catalytic oxidation requires elevated temperature and pressure, whereas electrochemical oxidation of HMF to FDCA, is possible at ambient conditions and can reduce the specific carbon footprint of the oxidation significantly.^{16,17} For the electrochemical oxidation, catalysts have been researched extensively.^{14,18} Transition metal catalysts such as Ni(OH)₂/NiOOH exhibit good selectivity^{19,20} and have been researched in depth.²¹ Latsuzbaia et al.²² demonstrated the potential of the synthesis route with a Ni(OH)₂/NiOOH catalyst in a lab-scale pilot plant with a yield of 70 %.

For an overall process, from the raw material (fructose) to the desired product (FDCA), the purification of HMF and the stability of HMF during oxidation are the most limiting steps.^{16,17,23} An approach to integrate these processes has been proposed by Liu et al.²⁴ It requires the dilution of the organic phase from HMF synthesis to a single aqueous phase. However, this impairs subsequent product separation and limits the reactant concentration.

An alternative could be the direct application of the organic intermediate phase in a biphasic electrochemical reactor. Biphasic electrochemical synthesis have already shown benefits when the product is *in-situ* extracted into a second phase to protect it from further oxidation.^{25,26}

This work studies the biphasic electrosynthesis to couple the electrochemical oxidation of HMF to FDCA and the dehydration of fructose to HMF as depicted in Scheme 1. It focuses on the biphasic electrochemical oxidation, where the raw organic product phase of an HMF synthesis is fed directly into an electrochemical flow-cell which mitigates the need for intermediate process separation. In the reactor, HMF is continuously extracted into the aqueous phase and oxidized with a $\text{Ni}(\text{OH})_2/\text{NiOOH}$ -coated nickel-foam electrode. After the synthesis, FDCA can be only found in the aqueous phase. We demonstrate the biphasic



Scheme 1: a) Process scheme of the integrated two-step synthesis, where fructose is dehydrated and extracted *in-situ* into an organic phase, which is fed into the electrochemical reactor, where HMF is oxidized to FDCA. b) Schematic of the electrochemical reactor. c) Schematic of the *in-situ* extraction of HMF from the organic phase in the electrochemical cell and the oxidation mechanism on the electrode.

direct conversion of an HMF feed from fructose dehydration. Subsequently we analyze the influence of the phase ratio (V_{Organic} to V_{Aqueous}) and current density for the biphasic

electrochemical oxidation with a model solution. Finally, we focus on the energy efficiency of the electrochemical oxidation by reducing the gap width of the flow-cell.

Experimental

Preparation of Electrodes

Nickel foam electrodes (grade 4753, Recemat NL) were prepared by deposition of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ catalyst following Aghazadeh et al.²⁷ Prior to deposition, electrodes were etched with a procedure from Garden et al.²⁸ A detailed description can be found in the SI.

Flow-Cell Experiments

Flow-cell experiments were conducted in a commercially available flex-E-cell (flex-X-cell GbR, Germany) with 35 cm^2 electrode area in an undivided cell. A more detailed description of the interior of the cell can be found in the SI. Schematic 1 b) shows the experimental process. Experiments for the validation of a process were conducted with 300 mL, further experiments with 450 mL of electrolyte. Reference experiments were conducted with an HMF concentration of 16.66 mmol L^{-1} HMF in 0.1 M KOH. In biphasic experiments, HMF was supplied with 50 mmol L^{-1} in the organic phase (2-MTHF). The aqueous phase (0.1 M KOH in DI-Water) was mixed with the organic phase according to the volume ratio ($V_{\text{Organic}}/V_{\text{Aqueous}}$) and continuously stirred with a propeller stirrer (C378-17-A, BOLA, Germany, EUROSTAR 40 IKA, GERMANY) and a ground clearance of 2 cm at 250 rpm. The emulsion was then pumped through the flow-cell by a gear pump (MCP-Z-Standard, Ismatec, Germany) at flow rates between 150 and 900 mL min^{-1} . pH and temperature were continuously monitored with a pH sensor (SE554, Knick, Germany). Power was supplied by a potentiostat (VMP150, VMP 3B-20 (20A/20V), Biologic) and the cell voltage was recorded. All experiments were carried out at room temperature. At current densities of 45 mA cm^{-2} and above, the reservoir temperature was controlled with a thermostat (CORIO CD-900F).

Samples were taken over the course experiments and analyzed via high performance liquid chromatography (HPLC). A detailed description can be found in the SI.

All experiments were evaluated for conversion (X), yield (Y), selectivity (S) and Faraday efficiency (FE), when 1 Faraday equivalent of charge in reference to the amount of HMF in the system was passed through the electrode. The corresponding calculations can be found in the SI. Consequently, this results in a shorter duration for experiments with higher current densities and a longer duration for experiments with a higher HMF content.

To evaluate the influence of the electrolyte gap on the cell voltage, the gap between the anode and the cathode was adjusted via the number of spacers. When the cell voltage is reported as a single value, it is the average value of the experiment, disregarding the first 10 % of reaction time.

Preparation of Raw Feed Solution from Fructose Dehydration

HMF synthesis was carried out using the batch reactor used in Aigner et al.¹³ The reaction was prepared according to the following protocol: 18.16 g of fructose are dissolved in 0.2 L of 0.2 mol L⁻¹ H₂SO₄. In addition, 236.67 g 2-MTHF are added to the system. The reactor was initially at room temperature and the velocity of the lower stirrer set to 400 rpm. Afterwards, the reactor was heated to 115 °C over a period of 125 min. The temperature was maintained for 30 min and quenched directly afterwards to stop the reaction. The organic and the aqueous phase were separated and stored at 4 °C. For better comparability of the results of the model solution with the feed from fructose dehydration, the HMF concentration in the raw HMF/2-MTHF solution from HMF synthesis was adjusted to 50 mmol L⁻¹ by diluting it with 2-MTHF. Experiments with the raw HMF/2-MTHF solution were then conducted similar to model solution experiments.

Results and Discussion

Process Validation

To show the feasibility of the biphasic electrochemical oxidation, we compare an experiment with the biphasic model solution to an experiment with an aqueous electrolyte with similar reaction conditions in Figure 1 a). The phase ratio in the biphasic experiment is 1:2 (V_{Organic} to V_{Aqueous}) at a current density of 15 mA cm^{-2} and a flow rate of 150 mL/min . The reaction

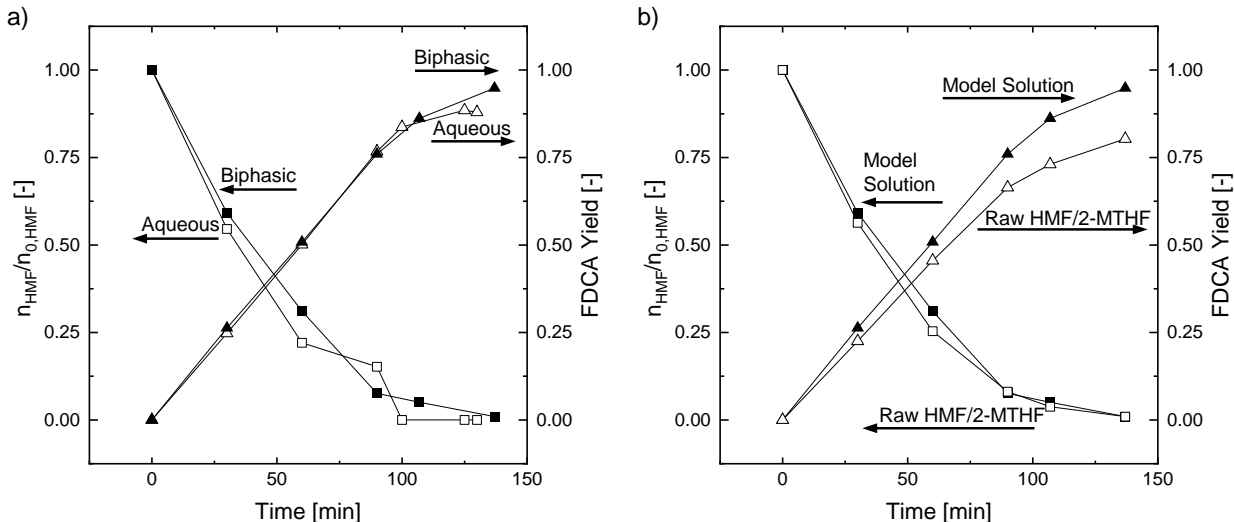


Figure 1: Comparison of the relative concentration of HMF and FDCA yield over the duration of the experiment for a) aqueous media (\square , \triangle) and the biphasic model solution (\blacksquare , \blacktriangle) and b) the biphasic model solution (\blacksquare , \blacktriangle) and HMF supplied via the raw HMF/2-MTHF solution from HMF synthesis (\square , \triangle).

rate of HMF appears higher in the purely aqueous system compared to the biphasic system, while the FDCA yield is very similar. This is most likely due to the degradation of HMF, reported in Figure S1 in the SI, which is decreased in the biphasic system. Full HMF conversion is not reached in the biphasic system, when 1 Faraday equivalent of charge is transferred after 105 min. This is most likely due to mass transport limitations, as HMF needs to diffuse from the organic to the aqueous phase before it can react at the electrode. Especially at low remaining HMF concentrations mass transfer will be low. Further, the electrode's surface is always partly in contact with the organic phase, which limits the available surface for the

aqueous oxidation. This effect has been described in literature in different systems.^{29,30}

While HMF can be found in both phases with a ratio of 1.4 ($n_{\text{HMF,org}}/n_{\text{HMF,aq}}$), FDCA is exclusively present in the aqueous phase due to its highly polar molecular configuration in alkaline environment. This effect eases the separation task after the experiments significantly. Moreover, the depletion of HMF, in case of full conversion, enables solvent recovery of 2-MTHF.

Figure 1 b) compares the biphasic model solution to an experiment with the raw HMF/2-MTHF solution from biphasic HMF synthesis. The raw HMF/2-MTHF solution from HMF synthesis contained impurities, recognizable by its brown color. The solution was used without any purification. When comparing the results, the HMF conversion is very similar to that of the model solution, but the FDCA yield is decreased by about 10%. We hypothesize that the decreased selectivity is mainly due to impurities from the HMF synthesis, where there is a broad spectrum of byproducts which cannot be detected in full, let alone quantified.

As intermediate HMF purification would require increased energy demand and suffer from HMF loss, the comparably low loss in FDCA yield is very promising for an integrated process concept.

Process Parameters

Different parameters influence the performance of the electrochemical process. Figure 2 shows the effect of the two most significant parameters: volume ratio of the aqueous and organic phase and current density. We did not see any significant effect of the electrolyte flow rate, which indicates that no mass transport limitation is apparent. The results are displayed in Figure S2 in the SI.

The ratio of organic and aqueous phase in Figure 2 a) influences the performance of the biphasic process significantly. Several effects have to be taken into account. The higher content of organic phase increases the reactant amount in the electrochemical cell, which

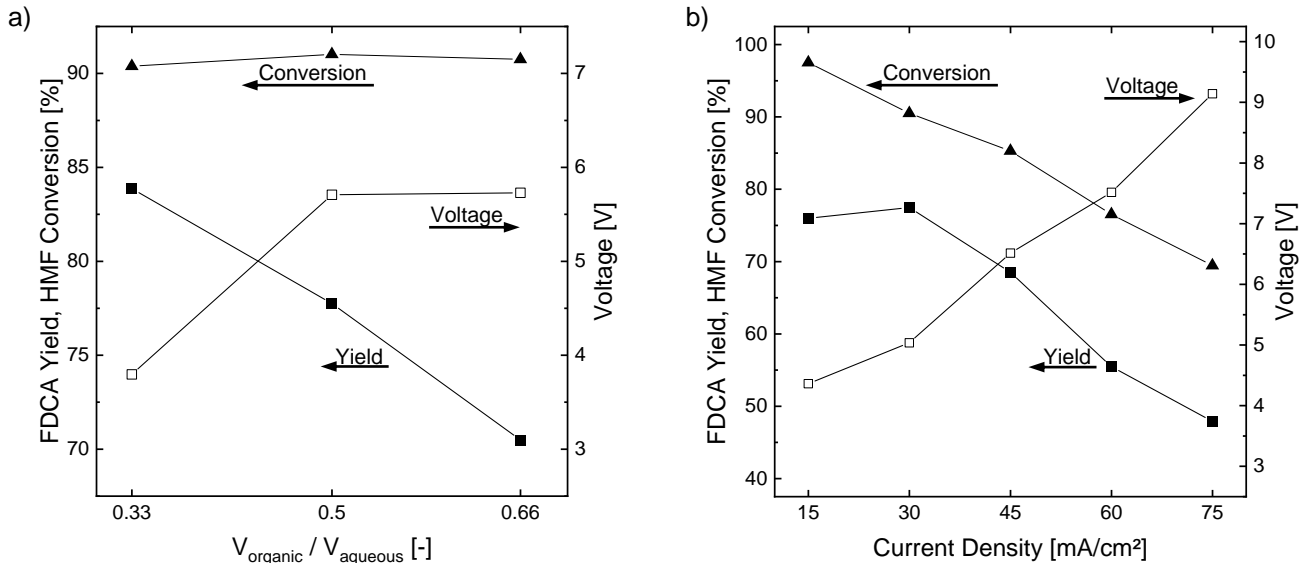


Figure 2: FDCA yield (■), HMF conversion (▲) (both on left y-axis) and cell voltage (□) (on right y-axis) at a) different volume ratios of the biphasic model electrolyte at 15 mA cm^{-2} and b) different current densities at a phase ratio of 1:2 ($V_{\text{aqueous}}:V_{\text{organic}}$) after a charge transfer corresponding to 1 FE.

is beneficial for a high electrochemical conversion rate. But the higher content of organic phase also increases cell voltage and blocks the available electrode surface area for the reaction.^{29,30} This interplay reflects in the results shown in Fig. 2 a). In total, all experiments show conversion rates above 90%. A higher ratio of organic phase increases the cell voltage and decreased the FDCA yield simultaneously. From an integrated process point of view, this results a trade-off: On the one hand, the total amount of HMF in the system (and by this the resulting concentration of FDCA in the aqueous phase) should be as high as possible, which is an argument for a high ratio of organic phase. On the other hand, yield should be maximized as well as cell voltage minimized, which is the case for lower ratio of organic phase. However, the cell voltage can be tackled by other means (see Section Cell Voltage below). When designing an economically feasible process, this trade-off needs to be matched appropriately. Therefore, we chose a phase ratio of 1:2 (V_{Organic} to V_{Aqueous}) for subsequent experiments to achieve a viable product concentration while retaining a high yield.

An important parameter for electrochemical process development is the current density as

it defines the production rate. Figure 2 b) shows the influence of the current density on the FDCA yield, the HMF conversion and the resulting cell voltage at a volume flow rate of 500 mL min^{-1} . The flow rate is increased in order to prevent mass transport limitations at higher current densities. With an increasing current density, the conversion drops from nearly 100 % at 15 mA cm^{-2} to 70 % at 75 mA cm^{-2} . $\text{Ni(OH)}_2/\text{NiOOH}$ is also a potent catalyst for oxygen evolution reaction (OER) in alkaline media, so that at an increasing current density OER will become a competing reaction. This is in accordance with a visibly increased gas evolution with increased current density. At 15 mA cm^{-2} and 30 mA cm^{-2} , the yield remains nearly unchanged between 75 % and 80 %. We attribute this to the decreased reaction time, which reduces the extend of the HMF degradation. At the higher current densities, this effect is superimposed by the decreased conversion, resulting in a lower overall yield. In the current experimental setup, a current density of 30 mA cm^{-2} appears to offer a good trade-off between sufficient conversion and short reaction time.

Further, it can be seen in Figure 2 b) that the cell voltage increases with increasing current density to over 9 V at 75 mA cm^{-2} , which is a consequence of the ohmic resistance of the electrolyte. The overall high cell voltage will impair the economic viability of this process. Therefore, the next section focuses on the reduction of cell voltage.

Cell Voltage

Previously, we showed a strong dependence of the cell voltage on the applied current density. Most of the increase is due to a high ohmic resistance in the electrolyte. One strategy to reduce this resistance is decreasing the electrolyte gap of the cell. Figure 3 shows the course of the cell voltage over the experiment duration with different gap width in the cell.

Independent of the gap widths, the cell voltage increases over the duration of the experiment. This is partly due to the depletion of the reactant HMF, while the product FDCA accumulates in the system. Further, with decreasing HMF concentration, OER is likely to

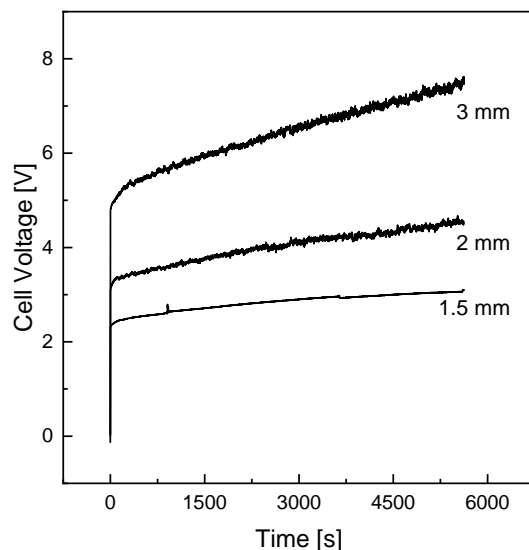


Figure 3: Cell voltage over the duration of three experiments for different gap widths of the flow channel at 30 mA cm^{-2} .

increase. However, most of the increase in voltage appears to be of an ohmic nature, as it shows a near linear relation to the overall cell voltage. It is far more pronounced at a gap width of 3 mm than at 1.5 mm. We speculate that this increase stems from the acidic nature of the product FDCA. This leads to a decrease in hydroxide ions. However, due to the logarithmic nature of the pH scale and the difficult measurement of the pH of biphasic electrolyte, this is not visible in pH measurements. For the gap width of 3 mm, the average voltage is around 6.5 V, which is most likely too high for an economically feasible process. We were able to decrease the cell voltage tremendously by decreasing the gap width, while yield and selectivity remained unaffected. We achieved the lowest cell voltage at a gap width of 1.5 mm and reduced the cell voltage, which is directly linked to the energy consumption, by over 50%. A further decrease of the gap width was not possible due to swelling of the EPDM frames, used to seal the flow channel. The swelling ultimately led to blocking of the flow channel at lower gap widths.

Conclusion and Outlook

In this work, we demonstrate an integrated process combining the biphasic chemo-catalytic synthesis of HMF from fructose with the subsequent electrochemical oxidation to FDCA without intermediate purification. The raw organic product phase is fed directly into the electrochemical flow-cell reactor where HMF is continuously extracted into the aqueous phase and oxidized to FDCA on a $\text{Ni}(\text{OH})_2/\text{NiOOH}$ anode. FDCA accumulates in the aqueous electrolyte, purifying the organic phase for its recycling. We demonstrate a viable process by comparing experiments with a real biphasic product mixture from fructose dehydration to biphasic model solution experiments and to a single phase electrochemical oxidation from literature. The biphasic electrochemical oxidation shows a yield of 85% with the model solution and close to 80%, when the raw HMF/2-MTHF solution from HMF synthesis is fed to the reactor without any purification.

With a model solution, we analyzed the influence of the phase ratio (V_{Organic} to V_{Aqueous}), where an increased ratio leads to an increased cell voltage and decreased selectivity. We increased the production rate by increasing the current density which resulted in an increased cell voltage and a decreasing FDCA yield with increasing current density above 30 mA cm^{-2} . Yet, the reaction time influences the yield significantly, due to the ever present degradation of HMF. We were able to decrease the cell voltage with smaller electrolyte gaps and thereby the direct energy input by over 50% by adjusting the cell design and gap width. This demonstrates a promising step towards an integrated synthesis of FDCA.

Future work should focus on two approaches: Firstly, a thorough analysis of the reaction in the biphasic electrolyte and secondly, an optimization on a process level. For the analysis of the reaction, the identification of unknown products from the HMF conversion from the raw HMF/2-MTHF solution is required. These could be unidentified oxidation products from e.g. ring-opening reactions but also unwanted products from a reduction reaction on the platinum cathode. If these are found, an ion exchange membrane, stable under these harsh conditions, could be necessary. On a process level, the entire process chain from hemi-cellulosic biomass

to FDCA should be assessed in a process model and optimized based on the experimental analysis presented here. A techno-economic assessment has to be conducted on the basis of the simulation to identify the economic potential of the coupled process for an integrated synthesis of FDCA from biomass.

Acknowledgement

M.W. acknowledges DFG funding through the Gottfried Wilhelm Leibniz Award 2019 [WE 4678/12-1]. M.W., T.H., M.P., F.B., D.R., J.L. and A.J. acknowledge funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – Exzellenzcluster 2186 „The Fuel Science Center“ – ID: 390919832”. This work was conducted in part at the Competence Center for Industrial Electrochemistry ELECTRA, which is supported by the “European Regional Development Fund (ERDF) and the Federal State of North Rhine-Westphalia (grant no. ERDF 05 00 07 7). The authors further thank Timo Linzenmeier for analytic work and Johanna Güttler, Katharina Weis and Lillian Büchel for experimental support.

Supporting Information Available

The following files are available free of charge.

- Supporting Information including tbd.

References

1. Geyer, R.; Jambeck, J. R.; Law, K. L. Production, use, and fate of all plastics ever made. *Science advances* **2017**, *3*, e1700782.

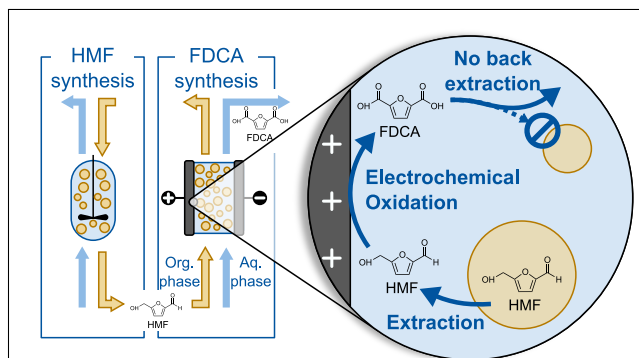
2. Meys, R.; Kätelhön, A.; Bachmann, M.; Winter, B.; Zibunas, C.; Suh, S.; Bardow, A. Achieving net-zero greenhouse gas emission plastics by a circular carbon economy. *Science (New York, N.Y.)* **2021**, *374*, 71–76.
3. Anastas, P.; Eghbali, N. Green chemistry: principles and practice. *Chemical Society reviews* **2010**, *39*, 301–312.
4. Zheng, J.; Suh, S. Strategies to reduce the global carbon footprint of plastics. *Nature Climate Change* **2019**, *9*, 374–378.
5. T. Werpy: Pacific Northwest National Laboratory;; G. Petersen: National Renewable Energy Laboratory, Top Value Added Chemicals from Biomass: Volume I–Results of Screening for Potential Candidates from Sugars and Synthesis Gas.
6. Zhang, H.; Jiang, M.; Wu, Y.; Li, L.; Wang, Z.; Wang, R.; Zhou, G. Development of High-Molecular-Weight Fully Renewable Biopolyesters Based on Oxabicyclic Diacid and 2,5-Furandicarboxylic Acid: Promising as Packaging and Medical Materials. *ACS Sustainable Chemistry & Engineering* **2021**,
7. de Jong, E.; Dam, M. A.; Sipos, L.; Gruter, G.-J. M. In *Biobased Monomers, Polymers, and Materials*; Smith, P. B., Gross, R. A., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 2012; Vol. 1105; pp 1–13.
8. Shen, T.; Zhang, B.; Wang, Y.; Yang, P.; Li, M.; Hu, R.; Guo, K.; Chen, K.; Zhu, N.; Wang, L.; Zhu, C.; Ying, H. Production of 100% bio-based semi-aromatic nylon by aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid with bio aliphatic diamine. *Chemical Engineering Journal* **2022**, *437*, 135361.
9. de Jong, E.; Visser, H. R. A.; Dias, A. S.; Harvey, C.; Gruter, G.-J. M. The Road to Bring FDCA and PEF to the Market. *Polymers* **2022**, *14*.

10. Rosenfeld, C.; Konnerth, J.; Sailer-Kronlachner, W.; Solt, P.; Rosenau, T.; van Herwijnen, H. W. G. Current Situation of the Challenging Scale-Up Development of Hydroxymethylfurfural Production. *ChemSusChem* **2020**, *13*, 3544–3564.
11. Mukherjee, A.; Dumont, M.-J.; Raghavan, V. Review: Sustainable production of hydroxymethylfurfural and levulinic acid: Challenges and opportunities. *Biomass and Bioenergy* **2015**, *72*, 143–183.
12. Saha, B.; Abu-Omar, M. M. Advances in 5-hydroxymethylfurfural production from biomass in biphasic solvents. *Green Chem* **2014**, *16*, 24–38.
13. Aigner, M.; Roth, D.; Rußkamp, J.; Klankermayer, J.; Jupke, A. Model-based equipment design for the biphasic production of 5-hydroxymethylfurfural in a tubular reactor. *AIChE Journal* **2020**, *66*, 1357.
14. Jensen, M. H.; Riisager, A. *Biomass, Biofuels, Biochemicals*; Elsevier, 2020; pp 135–170.
15. Sajid, M.; Zhao, X.; Liu, D. Production of 2,5-furandicarboxylic acid (FDCA) from 5-hydroxymethylfurfural (HMF): recent progress focusing on the chemical-catalytic routes. *Green Chemistry* **2018**, *20*, 5427–5453.
16. Patel, P.; Schwartz, D.; Wang, X.; Lin, R.; Ajao, O.; Seifitokaldani, A. Technoeconomic and Life-Cycle Assessment for Electrocatalytic Production of Furandicarboxylic Acid. *ACS Sustainable Chemistry & Engineering* **2022**, *10*, 4206–4217.
17. Massaro, M. C.; Monteverde, A. H. A. Techno-Economic Analysis of FDCA Production through Electrocatalytic Processes. *Journal of The Electrochemical Society* **2022**, *169*, 054515.
18. Ge, R.; Li, J.; Duan, H. Recent advances in non-noble electrocatalysts for oxidative valorization of biomass derivatives. *Science China Materials* **2022**, *488*, 294.

19. Grabowski, G.; Lewkowski, J.; Skowroński, R. The electrochemical oxidation of 5-hydroxymethylfurfural with the nickel oxide/hydroxide electrode. *Electrochimica Acta* **1991**, *36*, 1995.
20. Taitt, B. J.; Nam, D.-H.; Choi, K.-S. A Comparative Study of Nickel, Cobalt, and Iron Oxyhydroxide Anodes for the Electrochemical Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid. *ACS Catalysis* **2019**, *9*, 660–670.
21. Bender, M. T.; Choi, K.-S. Electrochemical Oxidation of HMF via Hydrogen Atom Transfer and Hydride Transfer on NiOOH and the Impact of NiOOH Composition on These Mechanisms. *ChemSusChem* **2022**,
22. Latsuzbaia, R.; Bisselink, R.; Anastasopol, A.; van der Meer, H.; van Heck, R.; Yagüe, M. S.; Zijlstra, M.; Roelands, M.; Crockatt, M.; Goetheer, E.; Giling, E. Continuous electrochemical oxidation of biomass derived 5-(hydroxymethyl)furfural into 2,5-furandicarboxylic acid. *Journal of Applied Electrochemistry* **2018**, *48*, 611–626.
23. Bello, S.; Salim, I.; Méndez-Trelles, P.; Rodil, E.; Feijoo, G.; Moreira, M. T. Environmental sustainability assessment of HMF and FDCA production from lignocellulosic biomass through life cycle assessment (LCA). *Holzforschung* **2019**, *73*, 105–115.
24. Liu, X.; Leong, D. C. Y.; Sun, Y. The production of valuable biopolymer precursors from fructose. *Green Chemistry* **2020**, *22*, 6531–6539.
25. Stiefel, S.; Lölsberg, J.; Kipshagen, L.; Möller-Gulland, R.; Wessling, M. Controlled depolymerization of lignin in an electrochemical membrane reactor. *Electrochemistry Communications* **2015**, *61*, 49–52.
26. Di Marino, D.; Aniko, V.; Stocco, A.; Kriescher, S.; Wessling, M. Emulsion electro-oxidation of kraft lignin. *Green Chemistry* **2017**, *19*, 4778–4784.

27. Aghazadeh, M.; Ghaemi, M.; Sabour, B.; Dalvand, S. Electrochemical preparation of α -Ni(OH)₂ ultrafine nanoparticles for high-performance supercapacitors. *Journal of Solid State Electrochemistry* **2014**, *18*, 1569–1584.
28. Grdeń, M.; Alsabet, M.; Jerkiewicz, G. Surface science and electrochemical analysis of nickel foams. *ACS applied materials & interfaces* **2012**, *4*, 3012–3021.
29. Liu, C.; Peljo, P.; Huang, X.; Cheng, W.; Wang, L.; Deng, H. Single Organic Droplet Collision Voltammogram via Electron Transfer Coupled Ion Transfer. *Analytical chemistry* **2017**, *89*, 9284–9291.
30. Zhang, H.; Sepunaru, L.; Sokolov, S. V.; Laborda, E.; Batchelor-McAuley, C.; Compton, R. G. Electrochemistry of single droplets of inverse (water-in-oil) emulsions. *Physical chemistry chemical physics : PCCP* **2017**, *19*, 15662–15666.

TOC Graphic



This work explores the biphasic electrochemical oxidation of HMF to FDCA and demonstrates the direct electrochemical conversion of the raw organic product phase of the HMF synthesis to FDCA.