

# Supporting Information:

## Integrated Biphasic Electrochemical Oxidation of HMF to FDCA

Tobias Harhues,<sup>†</sup> Maria Padligur,<sup>†</sup> Franziska Bertram,<sup>‡</sup> Daniel Roth,<sup>‡</sup> John Linkhorst,<sup>†</sup> Andreas Jupke,<sup>‡</sup> Matthias Wessling,<sup>†,¶</sup> and Robert Keller<sup>\*,†</sup>

<sup>†</sup>*RWTH Aachen University, Chemical Process Engineering, Forckenbeckstrasse 51, 52074 Aachen, Germany*

<sup>‡</sup>*RWTH Aachen University, Fluid Process Engineering, Forckenbeckstrasse 51, 52074 Aachen, Germany*

<sup>¶</sup>*DWI-Leibniz - Institute for Interactive Materials, Forckenbeckstrasse 50, 52074 Aachen, Germany*

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

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## Materials

Nickel foam (grade 4753) was purchased from Recemat NL, HMF (>99%) from AVA-Biochem. Nickelnitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and titanium foil (thickness 0.89 mm, 99.7% purity) were purchased from Alpha Aesar. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ,  $1 \text{ mol L}^{-1}$ ), nitric acid ( $\text{HNO}_3$ , 65 wt%), hydrochloric acid ( $\text{HCl}$ ,  $1 \text{ mol L}^{-1}$ ), FDCA (97%), 5-Hydroxymethyl-2-furancarboxylic acid (HMFCA) (<95%) and Furan-2,5-dicarbaldehyde (DFF) (97%) were purchased from Sigma-Aldrich. Aceton (technical), 2-MTHF (>99%), trifluoroacetic acid (TFA) ( $\geq 99.9\%$ ) and Acetic Acid (glacial, 100%) were purchased from CarlRoth. 2-formyl-5-furancarboxylic acid (FFCA) (<98%) was purchased from TCI chemicals. All chemicals were used as received without further purification.

## Preparation of Electrodes

Electrodes for the electrochemical cell were cut to a geometrical surface area of  $35 \text{ cm}^2$ . Prior to the deposition of the  $\text{Ni}(\text{OH})_2/\text{NiOOH}$  catalyst, nickel foams were etched with a procedure according to Garden et al.<sup>?</sup> to remove any contamination or oxide layers and increase the adhesion stability of the catalyst coating. After rinsing with deionized water (DI-water), the nickel foam electrodes were immersed in the etching solution for 10 min. The etching solution consisted of 40 ml DI-water, 50 ml 65 wt% nitric acid, 60 ml  $1 \text{ mol L}^{-1}$  sulfuric acid and 50 ml acetic acid. Subsequently, electrodes were rinsed with DI-water and cleaned in  $1 \text{ mol L}^{-1}$  hydrochloric acid and acetone in an ultrasonic bath for 15 min each and dried.

$\text{Ni}(\text{OH})_2/\text{NiOOH}$  catalyst coating was deposited following a procedure from Aghazadeh et al.<sup>?</sup> The cleaned electrodes were wetted with DI-water and subsequently immersed in a  $1 \text{ mol L}^{-1}$  solution of  $\text{Ni}(\text{NO}_3)_2$ . Then, a constant current of  $4.29 \text{ mA cm}^{-2}$  was applied for 15.5 min. A platinized titanium mesh (Umicore, Germany) with a surface area of  $35 \text{ cm}^2$  was used as the counter electrode.

## Flow-Cell assembly

The flex-E-cell was assembled the following way: Two layers of catalyst coated foam with a geometrical area of  $35\text{ cm}^2$  each were placed in the flow cell and contacted on the backside with a titanium plate. The electrolyte gap between anode and cathode was filled with a poly-propylene mesh spacer with a width of 0.8 cm. The counter electrode was a platinum coated titanium mesh (Umicore, Germany) on a titanium plate. Unless stated otherwise, the gap-size was 3 mm. Ion exchange membranes were not used as separator because of the challenging chemical environment of highly alkaline (pH 13) and organic media.

## Sampling and Sample Analysis

Samples were taken via a 3-way valve at the outlet of the flow cell in intervals of 15 min or 7.5 min in experiments with current densities of  $60\text{ mA cm}^{-2}$  and above. Samples were taken via 3 mL syringes, which were left upright for 5 minutes to allow for phase separation. Then, the phases were separated, separately diluted and prepared for high performance liquid chromatography (HPLC) analysis.

Liquid samples were then analyzed via HPLC. Aqueous samples were diluted tenfold, organic samples were diluted 20-fold. For the dilution, a phosphate buffer ( $7.5\text{ g L}^{-1}\text{ K}_2\text{HPO}_4$  and  $5.5\text{ g L}^{-1}\text{ KH}_2\text{PO}_4$ ) was used. An Agilent 1100 HPLC system with an organic acid resin column at  $35\text{ }^\circ\text{C}$  with a flow rate of  $1\text{ mL/min}$  at 90 bar column pressure was employed. The eluent was  $2\text{ mmol L}^{-1}$  TFA in purified water. Reactant concentrations were analyzed via diode-array detection: HMF and DFF were detected at 300 nm wavelength, FDCA, FFA and HMFCA were detected at 254 nm wavelength.

## Evaluation of Flow-Cell Experiments

Evaluation was done after 1 Faraday equivalent was passed through the electrode. The reaction time was calculated according to Eq. 1, where  $c$  is the concentration in  $\text{mol L}^{-1}$ ,  $V$  is the volume in L,  $z$  is the amount of required electrons for the reaction (6 for FDCA from HMF),  $F$  is the Faraday constant and  $I$  is the applied current in ampere.

$$t_{TC} = \frac{(c \cdot V) \cdot z \cdot F}{I} \quad (1)$$

Conversion ( $X$ ) of the substance  $i$  ( $X_i$ ) with a stoichiometric factor of 1 is calculated after Eq. 2, where  $n_{i,0}$  is the amount of substance  $i$  in the beginning of the experiment, and  $n_i$  is the amount of substance  $i$  at the time of evaluation.

$$X_i = \frac{n_{i,0} - n_i}{n_{i,0}} \quad (2)$$

Selectivity ( $S$ ) of the product  $j$  ( $S_j$ ) with a stoichiometric factor of 1 from the reactant  $i$  is calculated after Eq. 3.  $n_j$  is the amount of substance  $j$  at the time of evaluation,  $n_{i,0}$  is the amount of reactant  $i$  at the beginning of the experiment and  $n_i$  is the amount of reactant  $i$  at the time of evaluation.

$$S_j = \frac{n_j}{n_{i,0} - n_i} \quad (3)$$

Yield ( $Y$ ) of the product  $j$  ( $Y_j$ ) with a stoichiometric factor of 1 from the reactant  $i$  is calculated after Eq. 4.  $n_j$  is the amount of substance  $j$  at the time of evaluation and  $n_{i,0}$  is the amount of reactant  $i$  at the beginning of the experiment.

$$Y_j = \frac{n_j}{n_{i,0}} = S_j \cdot X_i \quad (4)$$

## HMF Degradation Experiments

HMF-degradation experiments were conducted in beaker experiments on a stirring plate at room temperature. For the degradation experiments with only aqueous or organic phase, the HMF concentration in the overall system was adjusted to match the concentration in the flow-cell experiments with a phase ratio of 1 to 2 (organic to aqueous phase), so that the HMF concentration was  $16.66 \text{ mol L}^{-1}$ . Degradation experiments with the biphasic mixture were conducted with a phase ratio of 1 to 2 (organic to aqueous phase). The mixture was stirred continuously with 300 rpm and samples were taken and processed similar to the flow-cell experiments.

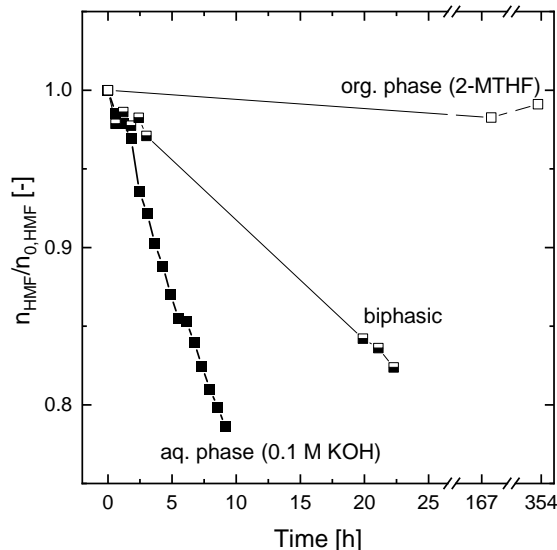


Figure S1: Degeneration of HMF in the aqueous electrolyte ( $0.1 \text{ mol L}^{-1}$  KOH), the organic phase (2-MTHF) and a 1:2 ( $V_{\text{Organic}}$  to  $V_{\text{Aqueous}}$ ) as used in future experiments. The initial HMF concentration was  $16.66 \text{ mmol L}^{-1}$ .

In the aqueous medium at pH 13, the experiments show a near linear HMF degradation. After 10 hours, more than 20% of the initial HMF is degraded, which is in agreement with literature.<sup>?</sup> In the organic phase, 2-MTHF exhibits no significant degradation over two weeks. This shows, that there is no need to extract HMF from the organic product phase to stabilize it for intermediate storage. In the biphasic mixture, HMF degeneration reduced

by more than 50% when compared to the single aqueous phase. Massaro et al. pointed out that the costs associated with HMF degradation are one of the critical parameters when processing HMF.<sup>?</sup> Especially in larger plants, where longer retention times could be necessary as larger volumes and amounts are processed, degradation will be even more prominent, and thus, the formation of humins will be even more problematic. In this regard, biphasic electrolytes are attractive as they increase the HMF stability.

## Influence of Flow Rate on FDCA Yield

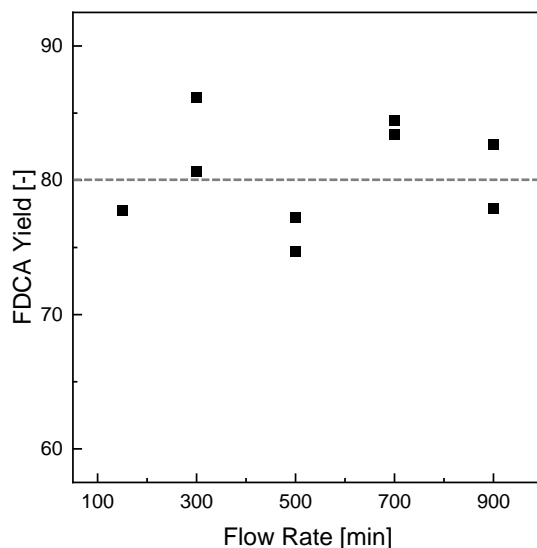


Figure S2: FDCA yield at different flow rates in the biphasic model solution ( $0.1 \text{ mol L}^{-1}$  KOH in the aqueous phase,  $50 \text{ mmol L}^{-1}$  HMF in the organic phase (2-MTHF) and a phase ratio of 1:2 ( $V_{\text{Organic}}$  to  $V_{\text{Aqueous}}$ ) at  $15 \text{ mA cm}^{-2}$  after a charge corresponding to 1 FE. Each data point represents a single experiment.