

# **VOLTA VOLTA**

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# Electrosynthesis of 2,5-furandicarboxylic acid

R.J.M. Bisselink, R. Latsuzbaia / roel.bisselink@tno.nl

TNO / Utrechtseweg 48 / 3704 HE Zeist / The Netherlands



# ---- INTRODUCTION

2-5-Furandicarboxylic acid (FDCA) is identified as important sugar-derived building block [1] and has the potential to replace terephtalic acid through, for example, production of polyethylene furanoate (PEF). PEF is considered a biobased alternative of polyethylene terephtalate (PET) having better gas barrier properties [2]. FDCA can be synthesised from 5-hydroxymethylfurfural (HMF) by various oxidation methods. Research focuses mainly on chemical catalysis while electrosynthesis is less explored [3]. Nonetheless, promising results are obtained with various electrocatalysts [4-7].

## --- OBJECTIVE

Previous research was done at HMF concentrations which are not suited for industrial processing. The objective of this research is to present a prospect for scaling up FDCA electrosynthesis and is therefore divided into:

1. Development of FDCA electrosynthesis

# **Table 1:** Electrolysis results obtained using NiOOH (pH 12.0) and TEMPO (pH 9.3) at 20°C in a divided cell under stirred conditions.

Electrocatalyst [-]	E <sub>anode</sub> 1 [V]	Cell [-]	[HMF] [mM]	Charge [F/mol]	CD <sup>2</sup> [mA/cm <sup>2</sup> ]	Х <sub>нмғ</sub> [%]	S <sub>fdca</sub> [%]	CE <sub>FDC</sub> / [%]
NiOOH (wire)	0.55	H-cell	50	4.2	3.1	98.5	60	84
NiOOH (foam <sup>3</sup> )	0.55	H-cell	250	6.9	3.5 (30)	99.4	90	78
NiOOH (foam³)	0.80	Flow-cell	650	6.7	1.7 (23)	100	89	80
NiOOH (foam³)	0.75	Flow-cell	750	6.1	2.0 (28)	100	82	80
15 mM TEMPO (wire)	0.75	H-cell	10	6.1	3.1	100	97	96
50 mM TEMPO (RVC <sup>3</sup> )	0.80	H-cell	100	6.3	2.2 (75)	98.4	89	84

### <sup>1</sup> vs. SCE (H-cell) and vs. Ag|AgCl (flow cell)

<sup>2</sup> denotes real current density, between brackets based on geometric surface
 <sup>3</sup> 30 p.p.i nickel foam and 100 p.p.i. reticulated vitreous carbon (RVC) were used

tion within 6 hours. Cyclic voltammograms were therefore recorded at pH 12 with NiOOH and pH 9.3 (similar to [7]) for TEMPO (Figure 1). TEMPO exhibits a better activity compared to NiOOH. Preparative electrolysis shows however similar current densities (Table 1), possibly the result of different oxidation rates of HMF and intermediates with the electrocatalyst which is indicated by HMF conversion and selectivity of FDCA and intermediates during electrolysis (Figure 3 and [7]). Utilisation of 3D electrodes increases the geometric current density towards industrial levels enabling almost full HMF conversion in the H-cell. A molar yield (conversion x selectivity) of 90% was obtained with NiOOH, which is higher than previously reported, 71% at pH 14 [4]. This difference in yield is attributed to HMF degradation (19%) in 4 hours at pH 14). Near to quantitative conversion of HMF to FDCA with TEMPO confirms results of Cha et al. [7]. The use of 3D electrode material (RVC) increased current density similar to NiOOH. Higher selectivities and yields were obtained with TEMPO. Further experiments with increased HMF concentrations were done with NiOOH as it enables less complex processing downstream. Full conversion of 0.65 and 0.75 M HMF in a 100 cm<sup>2</sup> plate-and-frame cell resulted in very good yields of FDCA (Table 1) with an associated energy usage of 3.4 kWh/kg FDCA.





- using higher HMF concentrations with full HMF conversion.
- 2. Demonstration of FDCA electrosynthesis combined with downstream processing.

## ---- RESULTS

Cyclic voltammetry and preparative electrolysis indicated NiOOH and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) electrocatalysts to be more advantageous over Pt, Au and Au<sub>3</sub>Pd<sub>2</sub> in alkaline solutions due to better catalyst activity, catalyst stability and FDCA selectivity. HMF degrades in strong alkaline solutions [5].

At pH  $\leq$  12.5 we found no significant HMF degrada-





**Figure 3:** HMF conversion and selectivity of FDCA and intermediates during electrolysis in a divided cell at **A**: NiOOH with 650 mM HMF, 0.02 M phosphate buffer (pH = 12), 0.3 M NaClO<sub>4</sub> at 0.8 V vs. SCE and **B**: Au with 10 mM HMF, 15 mM TEMPO, 0.1 M borate buffer (pH = 9.3), 0.3 M NaClO<sub>4</sub> at 0.75 V vs. SCE.

# --- CONCLUSION & OUTLOOK

Electrosynthesis of FDCA from HMF using NiOOH and TEMPO electrocatalysts resulted in very good to near quantitative FDCA yields. Utilisation of 3D foam electrodes increased geometrical current density significantly and were used to demonstrate FDCA electrosynthesis at industrial relevant concentrations.

Next step in our research is the development of an electrochemical system in which electrosynthesis and downstream processing are combined.

**Figure 1:** Cyclic voltammograms at 10 mV/s of 15 mM TEMPO in 0.1 M borate buffer (pH 9.3) with 0.3 M NaClO<sub>4</sub> with 10 mM HMF and NiOOH in 0.02 M phosphate buffer (pH 12) with 0.3 M NaClO<sub>4</sub> with 10 mM HMF.

**Figure 2:** 100 ml H-cell used for preparative electrolysis, controlled by a potentiat (Ivium instruments).

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