

Electroreduction of Furfural on a Diamond Electrode

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In recent years, biomass has attracted attention as a raw material for sustainable material production [1]. In addition, electro-organic synthesis has attracted attention as a clean technology that does not involve excess reagent waste, as the reaction is initiated by electron transfer on the electrodes. Along these lines, we aimed to convert biomass-derived material into a fuel precursor: electroreduction of furfural to furfuryl alcohol.

Constant current electrolysis was performed in an undivided batch cell: furfural (**1**; 0.1 M), MeOH (5.0 mL), 0.50 mA/cm², 400 rpm, and rt. Supporting electrolytes, electrode materials, and the amount of charge (referring to **1**) were screened to optimize reaction conditions. Products were identified by gas chromatography-mass spectrometry (GC-MS).

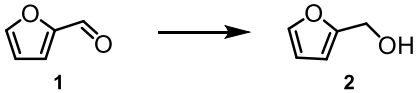
Electroreduction of **1** produced furfuryl alcohol (**2**). The highest GC-MS yield of **2** was 21% under optimum conditions: (anode) graphite, (cathode) boron-doped diamond (BDD), (supporting electrolyte) KOH (0.15 M), (current density) 2.0 mA/cm², and (amount of charge) 4.0 F (referring to **1**) (**Table 1**, entry 8). For a supporting electrolyte, not only the inorganic salt (KOH) but also the organic salt (Bu₄NOH) was investigated, indicating that the size of cation species of supporting electrolytes affects the yield of **2**. It is noted that this tendency is also observed in the previous study of microflow electrolysis of **1** [2]. In terms of the amount of charge, GC-MS yields were high when the amount of charge was greater than 2.0 F. Since the present reaction is assumed to be a two-electron reaction, it is suggested that a side reaction to afford 2-furoic acid methyl ester (**3**) is proceeded (**Scheme 1**).

References

[1] J. A. Schaidle, A. Holewinski et al., *ACS Energy Lett.* **6** (2021), 1205.

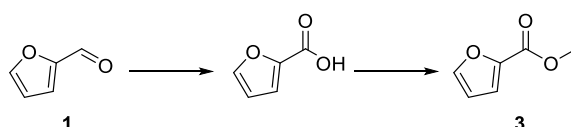
[2] Y. Cao, T. Noël, *Org. Process Res. Dev.* **23** (2019), 403.

Table 1. Screening of reaction conditions.



Electrode, Supporting electrolyte, Amount of charge (referring to **1**), Current density, MeOH, rt.

Entry	Electrode Anode / Cathode	Supporting electrolyte	Amount of charge (referring to 1)	Current density	GC-MS yields	
					1 / %	2 / %
1	Cu / BDD	Bu ₄ NOH	2.0 F	2.0 mA/cm ²	43	4
2	Cu / BDD	KOH	2.0 F	2.0 mA/cm ²	36	13
3	Graphite / BDD	KOH	2.0 F	2.0 mA/cm ²	28	15
4	Graphite / BDD	KOH	1.0 F	2.0 mA/cm ²	21	13
5	Graphite / BDD	KOH	4.0 F	2.0 mA/cm ²	30	18
6	Graphite / BDD	KOH	4.0 F	0.50 mA/cm ²	37	21



Scheme 1. Plausible side reaction in the electroreduction of furfural (**1**).