

Supporting Information

Exploring the Electrochemical Ring Hydrogenation of Furanic Compounds

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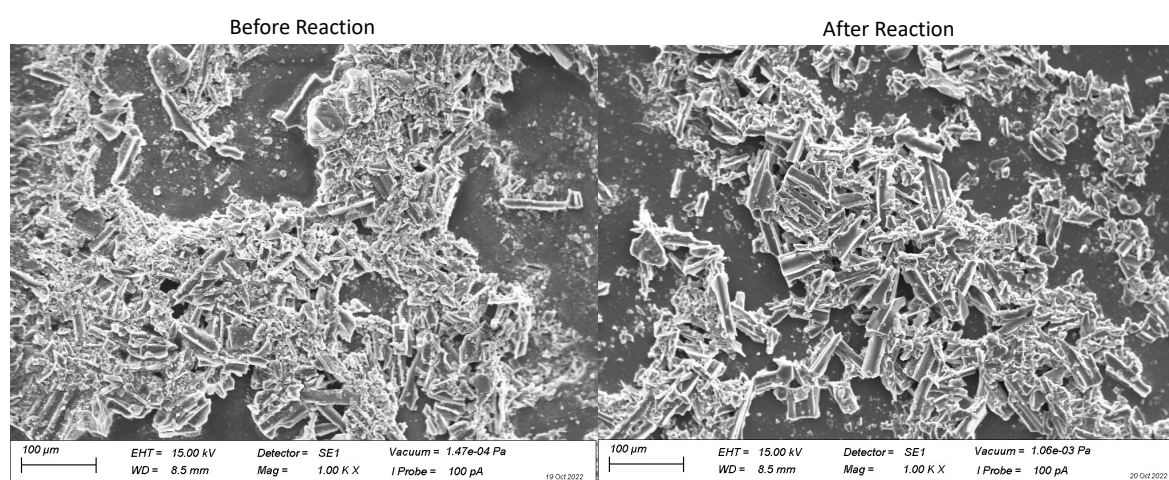


Figure S1: SEM images of the Pd:Pt 5:1 electrode material as an example for the surface morphology of ink-deposited electrodes before and after the reaction.

Table S1: Results of the EDX analysis of Pd:Pt 5:1 electrode material as an example for the electrode constitution before a reaction.

Element	Weight%	Atom%	Net. Int.	Error %	P/B Ratio	R	F
C K	58.7	70.8	3967.1	11.5	0	1.0000	1.0000
O K	5.9	5.3	156.7	28.2	0	1.0000	1.0000
F K	30.2	23.0	2714.4	20.5	0	1.0000	1.0000
S K	0.5	0.2	105.9	1.3	7.776216	1.0114	1.0186
PdL	4.3	0.6	401.3	0.8	58.9214	1.0138	1.0036
PtL	0.4	0.0	5.0	11.5	3.58999	1.0276	1.0762

Table S2: Results of the EDX analysis of Pd:Pt 5:1 electrode material as an example for the electrode constitution after a reaction.

Element	Weight%	Atom%	Net. Int.	Error %	P/B Ratio	R	F
C K	70.3	79.9	5794.3	8.1	0	1.0000	1.0000
O K	8.2	7.0	191.9	27.5	0	1.0000	1.0000
F K	17.4	12.5	1318.2	24.6	0	1.0000	1.0000
S K	0.4	0.2	85.0	1.3	6.592108	1.0107	1.0199
PdL	3.5	0.5	337.6	0.8	49.98526	1.0129	1.0038
PtL	0.2	0.0	3.3	21.6	2.435824	1.0259	1.0819

Table S3: Compounds analyzed with HPLC and corresponding retention times using an HPLC (Agilent 1260 Infinity II LC, USA). A Phenomenex Hydro-RP 80 Å (4 µm, 250 x 4.6 mm) with an eluent flow rate of 1 mL/min at 25°C using a 1:1 mixture of deionized water and acetonitrile was used.

Compound	Retention time [min]
Furfural	3.79
Furfuryl alcohol	3.15
2-Methylfuran	8.65
Tetrahydrofurfuryl alcohol	2.78
Methyl tetrahydrofuran	5.88
Furoic acid	2.89
Furan	6.43
Tetrahydrofuran	4.70

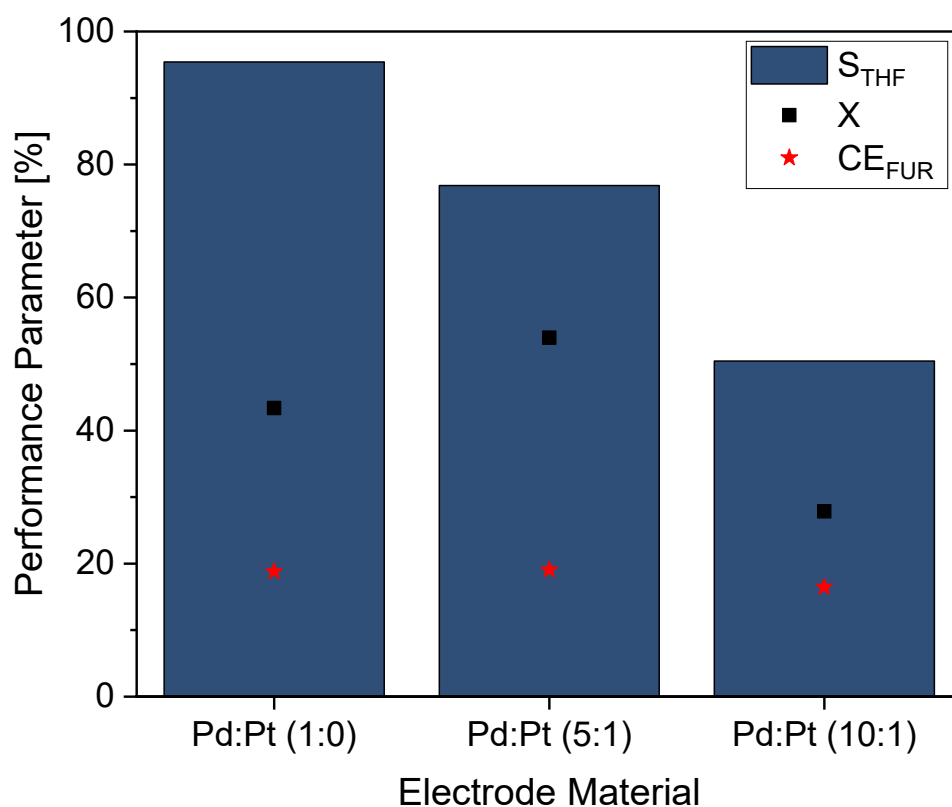


Figure S2: Comparison of selected reaction performance parameters for utilizing different electrode materials for FUR as starting material with 2 FEq (Faraday Equivalents) transferred charge / 26.9 min with -300 mA. Due to the high vapor pressure and boiling temperature of the compounds the concentration determination was impaired.

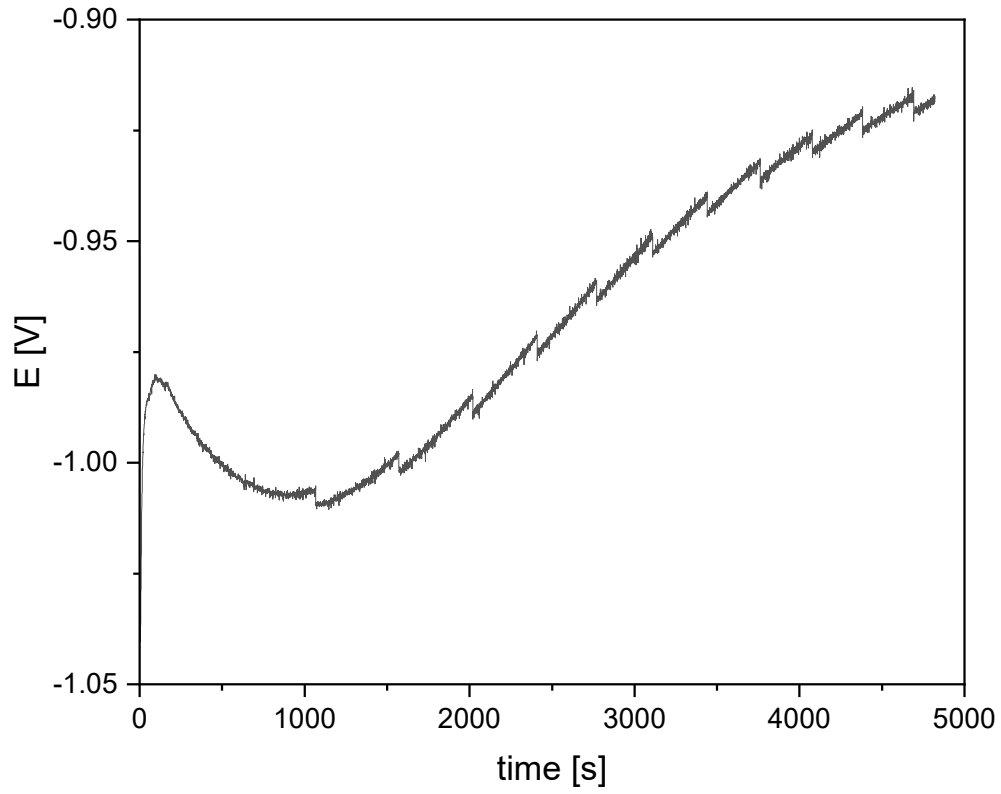


Figure S3: Exemplary plot of potential vs. Ag/AgCl over time for Pd:Pt 10:1 with FF in 0.5 M H₂SO₄ with 15% acetonitrile.

$$X = \frac{n_{Educt,0} - n_{Educt,end}}{n_{Educt,0}} \cdot 100 \quad (S1)$$

$$S_{Product} = \frac{n_{Product,end}}{n_{Educt,0} - n_{Educt,end}} \cdot \frac{|v_{Educt}|}{v_{Product}} \cdot 100 \quad (S2)$$

$$CE_{product} = \frac{n_{Product,real}}{n_{Product,theoretical}} \cdot 100 \quad (S3)$$

Table S4: Concentration and reaction performance values for different transferred FEq using a platinized Pt electrode (Pt/Pt) as electrode material in 0.5 M H₂SO₄ electrolyte with FF as starting material.

FE q	Time [min]	Charge [C]	C _{OFEq, FF} [mM]	S ² (C _{O,FF})	C _{6FEq, FF} [mM]	S ² (C _{FF})	X [%]	C _{6FEq, FA} [mM]	S ² (C _{FA})	C _{6FEq, MF} [mM]	S ² (C _{MF})	C _{6FEq, THFA} [mM]	S ² (C _{THFA})	MB [%]	S _{6FEq, FA} [%]	S _{6FEq, MF} [%]	S _{6FEq,THFA} [%]	CE _{6FEq,FA} [%]	CE _{6FEq, MF} [%]	CE _{6FEq,THF_A} [%]	CE _{total} [%]
2	26.8	482.43	51.30	1.45	44.12	1.58	13.99	1.72	0.00	0.89	0.05	0.43	0.0001	91.94	23.94	12.42	6.03	3.43	3.57	2.59	9.60
4	53.6	964.85	51.30	1.45	39.61	1.97	22.79	2.61	0.11	1.22	0.06	0.59	0.0009	85.82	22.36	10.45	5.03	2.61	2.45	1.76	6.82
6	80.4	1447.3	51.30	1.45	36.10	0.32	29.61	3.14	0.09	1.21	0.10	0.70	0.0040	80.22	20.64	7.98	4.61	2.09	1.61	1.40	5.10
8	107.2	1929.7	51.30	1.45	33.39	0.00	34.89	3.46	0.03	1.55	0.05	0.79	0.0063	76.41	19.35	8.82	4.42	1.73	1.55	1.19	4.47

Table S5: Concentration and reaction performance values for different electrode materials with 6 tranferred FE in 0.5 M H₂SO₄ electrolyte with FF as starting material.

WE material	C _{OFEq, FF} [mM]	S ² (C _{O,FF})	C _{6FEq, FF} [mM]	S ² (C _{FF})	X [%]	C _{6FEq, FA} [mM]	S ² (C _{FA})	C _{6FEq, MF} [mM]	S ² (C _{MF})	C _{6FEq, THFA} [mM]	S ² (C _{THFA})	MB [%]	S _{6FEq, FA} [%]	S _{6FEq, MF} [%]	S _{6FEq,THFA} [%]	CE _{6FEq, FA} [%]	CE _{6FEq, MF} [%]	CE _{6FEq,THF_A} [%]	CE _{total} [%]
GC	52.21	0.13	17.42	35.7	66.63	12.24	39.5	0.33	0.06	0.00	0.00	57.48	34.14	1.00	0.00	8.16	0.44	0.00	8.60
Pd	51.79	0.26	35.67	1.38	31.13	14.33	1.80	0.32	0.007	0.22	0.00	97.59	88.79	2.01	1.35	9.55	0.43	0.43	10.41
Pt	52.12	0.08	48.72	0.00	6.52	0.93	0.01	0.26	0.002	0.00	0.00	95.77	27.43	7.81	0.00	0.62	0.35	0.00	0.97
PtPt	51.30	1.45	36.10	0.32	29.61	3.14	0.09	1.21	0.10	0.70	0.004	80.22	20.64	7.98	4.61	2.09	1.61	1.40	5.10
Pd:Pt (1:1)	50.33	2.65	27.59	14.51	45.28	6.49	8.54	0.30	0.03	3.06	0.01	74.22	29.29	1.38	13.51	4.33	0.41	6.12	10.86
Pd:Pt (1:5)	50.23	0.07	33.07	8.62	34.17	7.12	2.25	0.30	0.0004	1.50	0.000	83.59	42.69	1.81	8.85	4.75	0.41	3.00	8.15
Pd:Pt (1:10)	51.10	1.14	38.19	0.1	25.26	2.83	2.90	0.24	0.002	0.41	0.004	81.50	21.56	1.83	3.16	1.89	0.32	0.81	3.01
Pd:Pt (5:1)	50.64	1.02	24.54	0.89	51.55	9.39	0.04	0.30	0.003	4.00	0.02	75.48	35.96	1.16	15.33	6.26	0.40	8.00	14.67
Pd:Pt (10:1)	49.81	0.02	23.15	8.32	53.53	9.77	3.35	0.26	0.003	3.35	0.40	73.33	37.22	0.98	12.51	6.52	0.34	6.70	13.56
Pd:Pt (0:1)	49.66	0.79	37.50	118.6	24.67	3.54	0.07	0.27	0.03	0.00	0.00	83.00	42.63	4.22	0.00	2.36	0.36	0.00	2.72
Pd:Pt (1:0)	49.86	0.37	25.91	0.12	48.02	9.42	13.9	0.36	0.09	2.76	0.72	77.08	39.07	1.48	11.46	6.28	0.48	5.52	12.06

Table S6: Concentration and reaction performance values for the second utilization of different electrode materials with 6 tranferred FE in 0.5 M H₂SO₄ electrolyte with FF as starting material.

WE material	C _{0FEq, FF} [mM]	S ² (C _{0,FF})	C _{6FEq, FF} [mM]	S ² (C _{FF})	X [%]	C _{6FEq, FA} [mM]	S ² (C _{FA})	C _{6FEq, MF} [mM]	S ² (C _{MF})	C _{6FEq, THFA} [mM]	S ² (C _{THFA})	MB [%]	S _{6FEq, FA} [%]	S _{6FEq, MF} [%]	S _{6FEq, THFA} [%]	CE _{6FEq, FA} [%]	CE _{6FEq, MF} [%]	CE _{6FEq, THFA} [%]	CE _{total} [%]
Pd:Pt (0:1)	50.41	1.41	37.94	89.9	24.95	2.34	0.66	0.22	0.02	0	0.00	80.11	26.93	2.76	0	1.56	0.30	0	1.86
Pd:Pt (1:10)	51.22	5.19	39.33	3.40	23.23	3.41	0.14	0.22	0.0001	0.21	5x10 ⁻⁵	84.27	28.67	1.85	1.78	2.28	0.29	0.42	2.99
Pd:Pt (1:5)	50.31	0.002	38.34	56.4	23.79	5.69	20.1	0.27	0.001	0.50	0.18	89.03	44.54	2.67	3.82	3.79	0.35	1.00	5.15
Pd:Pt (1:1)	49.79	0.91	34.08	6.79	31.60	5.23	7.91	0.21	0.01	1.27	0.05	81.82	34.39	1.40	8.20	3.48	0.29	2.54	6.31
Pd:Pt (5:1)	51.72	2.22	30.44	20.9	40.99	9.50	10.1	0.28	0.003	2.47	4.41	82.55	44.32	1.33	10.63	6.33	0.37	4.94	11.65
Pd:Pt (10:1)	50.42	3.61	24.48	16.2	51.56	9.43	0.01	0.25	0.0003	3.19	4.53	74.09	36.48	0.98	12.02	6.29	0.34	6.39	13.02
Pd:Pt (1:0)	50.10	1.39	27.04	1.98	46.03	8.17	9.00	0.21	0.01	2.57	0.37	75.78	35.49	0.91	11.16	3.63	0.20	2.45	6.28

Table S7: Concentration and reaction performance values for the utilization of different electrode materials with 6 tranferred FE in 0.5 M HCl electrolyte with FF as starting material.

WE material	C _{0FEq, FF} [mM]	S ² (C _{0,FF})	C _{6FEq, FF} [mM]	S ² (C _{FF})	X [%]	C _{6FEq, FA} [mM]	S ² (C _{FA})	C _{6FEq, MF} [mM]	S ² (C _{MF})	C _{6FEq, THFA} [mM]	S ² (C _{THFA})	MB [%]	S _{6FEq, FA} [%]	S _{6FEq, MF} [%]	S _{6FEq, THFA} [%]	CE _{6FEq, FA} [%]	CE _{6FEq, MF} [%]	CE _{6FEq, THFA} [%]	CE _{total} [%]
Pd:Pt (1:0)	50.45	0.29	21.84	9.21	56.71	15.88	1.43	1.649	0.004	2.79	3.19	83.58	55.52	5.76	9.76	10.59	2.20	5.59	18.37
Pd:Pt (5:1)	49.58	0.25	18.27	3.04	63.16	14.27	0.12	1.32	0.002	1.00	0.06	70.30	45.57	4.22	3.18	0.88	19.02	1.99	21.9
Pd:Pt (10:1)	49.45	0.01	14.97	3.09	69.76	13.57	9.21	0.89	0.002	1.32	0.52	62.10	39.29	2.56	3.83	9.04	1.18	2.65	12.86

Table S8: Concentration and reaction performance values for the utilization of different electrode materials with 6 tranferred FE in 0.5 M H₂SO₄ electrolyte with FA as starting material.

WE material	C _{0FEq, FA} [mM]	s ² (c _{0,FF})	C _{6FEq, FA} [mM]	s ² (c _{FF})	X [%]	C _{6FEq, MF} [mM]	s ² (c _{MF})	C _{6FEq, THFA} [mM]	s ² (c _{THFA})	MB [%]	S _{6FEq, MF} [%]	S _{6FEq, THFA} [%]	CE _{6FEq, MF} [%]	CE _{6FEq, THFA} [%]	CE _{total} [%]
Pd:Pt (1:0)	44.21	12.44	28.92	3.64	34.52	0.41	0.01	2.94	0.18	73.04	2.65	19.33	0.27	3.92	4.19
Pd:Pt (5:1)	44.25	11.58	27.91	8.81	36.96	0.38	0.01	3.82	0.18	76.48	2.30	23.74	0.25	5.10	5.35
Pd:Pt (10:1)	40.61	46.60	28.74	18.92	29.13	0.35	0.01	3.97	0.25	81.53	2.92	33.72	0.23	5.29	5.52

Table S9: Concentration and reaction performance values for the utilization of different electrode materials with 4 tranferred FE in 0.5 M H₂SO₄ electrolyte with FUR as starting material. N.a.* = not applicable as for furan only a unicat experiment was performed.

WE material	C _{0FEq, FUR} [mM]	s ² (c _{0,FUR})	C _{6FEq,FUR} [mM]	s ² (c _{FUR})	X [%]	C _{6FEq, THF} [mM]	s ² (c _{THF})	MB [%]	S _{6FEq, THF} [%]	CE _{6FEq, THF} [%]
Pd:Pt (1:0)	11.36	n.a.*	6.43	n.a.*	43.38	4.7	n.a.*	98.00	95.41	18.80
Pd:Pt (5:1)	11.50	n.a.*	5.30	n.a.*	53.95	4.77	n.a.*	87.5	76.83	19.06
Pd:Pt (10:1)	29.30	n.a.*	21.14	n.a.*	27.85	4.12	n.a.*	86.20	50.45	16.46