Cutting the overpotential of electrochemical hydrogenations for enhanced hydrogenation efficiency

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Supporting Information

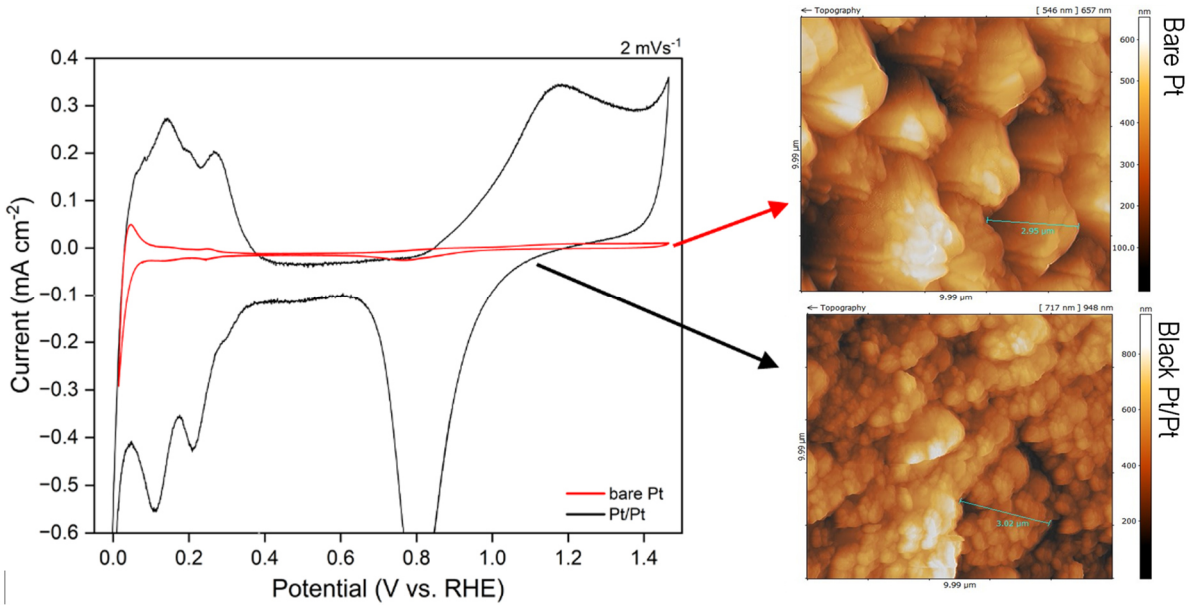

Fig. SI 1: Comparison of Platinum electrode before and after electrodeposition with Pt black: CV (A) of bare Pt (red) and platinized Pt (black); and the AFM images (B) of respective electrodes.

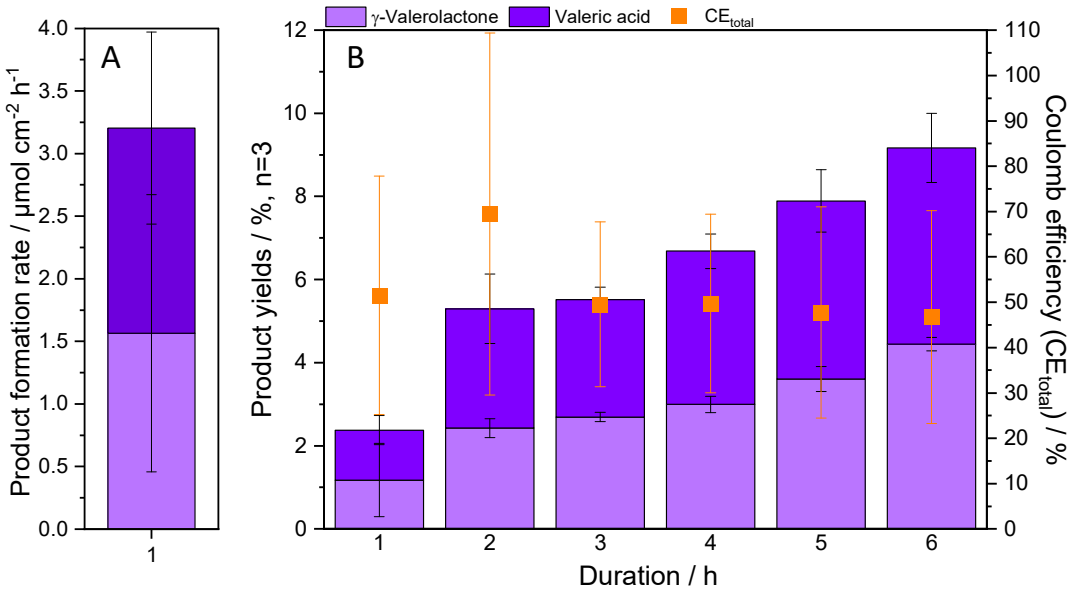

Fig. SI 2: Product formation rate (A) of the electrolysis of 10 mM levulinic acid in 0.1 M $HClO_4$ at Pt/Pt, determined after 1-helectrolysis. Time dependence of the product yields (B) and the Coulomb efficiency during a 6-hour electrolysis. The electrolyses were performed at 20 °C, at a potential of +0.015 V (vs. RHE).

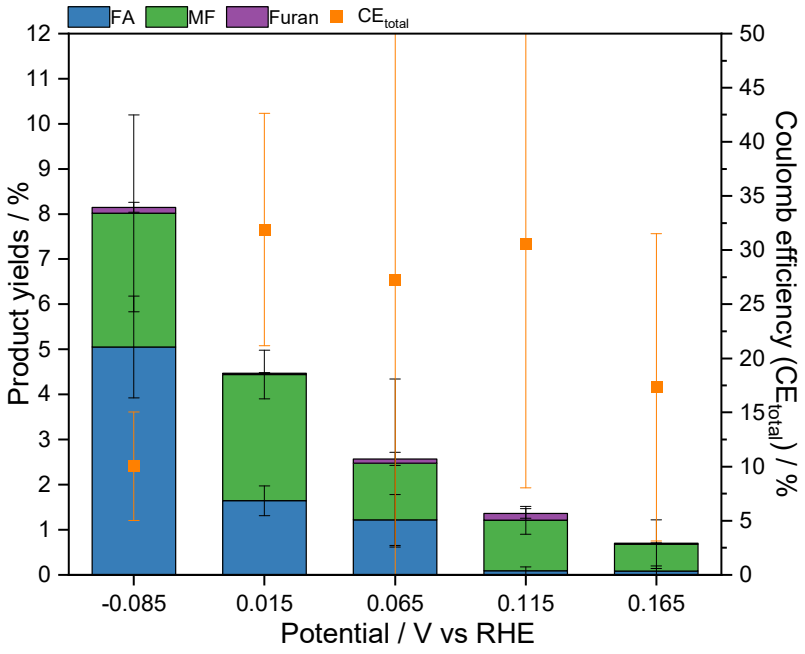

Fig. SI 3: Electrolysis results of 1-h potentiostatic electrolysis experiments using 10 mM furfural solutions in 0.1 M $HClO_4$ at a temperature of 20 °C and performed at different electrode potentials.

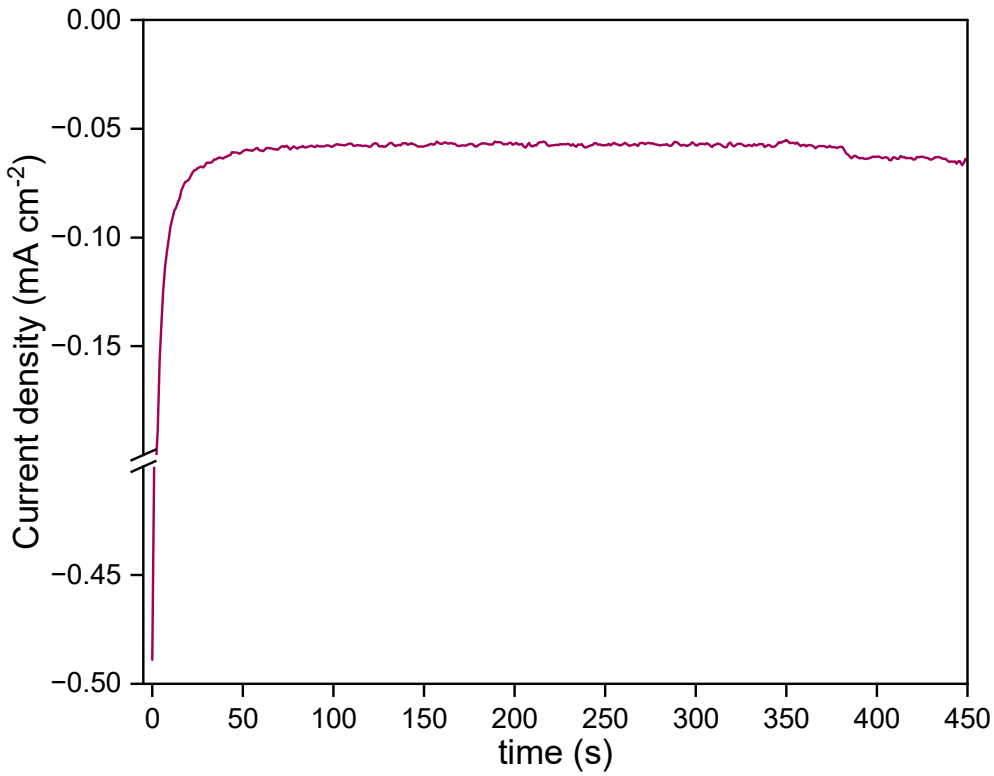

Fig. SI 4 Chronoamperometric plot of Pt/Pt in 0.1 M $HClO_4$ (without addition of organic reactant) at an applied potential of +0.165 V vs. RHE stirred at 300 RPM, 20 °C.

Table SI 1. Performance parameters for the ECH of 10 mM levulinic acid at 20°C and 50°C for 6-h electrolysis at 300 rpm. E_{app}=+0.015 V vs RHE. WE: Pt/Pt, CE: Pt, RE: Ag/AgCl (sat'd KCl). n=3

MEAN	time	ΔQ	% $C_{balance}$	$c_{\gamma\text{-VL}}$ mM	Product formation rate$_{\gamma\text{-VL}}$ µmol h^{-1} cm^{-2}	% Yield$_{\gamma\text{-VL}}$	% CE$_{\gamma\text{-VL}}$	c_{VA} mM	Product formation rate$_{VA}$ µmol h^{-1} cm^{-2}	% Yield$_{VA}$	% CE$_{VA}$	% CE$_{total}$
20°C	1	15.04	90.41	0.26	1.56	1.18	16.45	0.27	1.64	1.20	35.05	51.51
	2	26.17	99.10	0.51	1.56	2.43	19.56	0.64	1.93	2.87	49.91	69.47
	3	34.17	91.18	0.57	1.11	2.69	15.56	0.61	1.20	2.82	33.97	49.53
	4	41.70	91.59	0.64	0.93	3.00	14.19	0.80	1.15	3.69	35.52	49.71
	5	51.67	92.50	0.78	0.87	3.61	13.83	0.94	1.06	4.28	33.94	47.77
	6	59.70	93.45	0.95	0.87	4.45	14.47	1.04	0.95	4.72	32.23	46.70
50°C	1	19.42	107.17	0.62	3.77	3.15	49.19	0.43	2.63	2.05	60.48	76.34
	2	42.07	99.40	1.04	3.11	4.50	27.40	0.80	2.40	3.33	30.24	57.64
	3	59.60	101.69	1.28	2.50	5.68	20.34	0.89	1.74	3.76	24.26	44.60
	4	80.00	91.44	1.47	2.11	6.38	15.45	1.01	1.45	4.20	19.27	34.73
	5	105.83	91.42	1.58	1.78	6.96	12.53	0.96	1.08	4.04	13.92	26.46
	6	126.25	75.19	1.87	1.71	8.20	12.06	1.09	1.00	4.60	13.08	25.13
STD DEV	time	ΔQ	$C_{balance}$ %	$c_{\gamma\text{-VL}}$ mM	Product formation rate$_{\gamma\text{-VL}}$ µmol h^{-1} cm^{-2}	% Yield$_{\gamma\text{-VL}}$	% CE$_{\gamma\text{-VL}}$	c_{VA} mM	Product formation rate$_{VA}$ µmol h^{-1} cm^{-2}	% Yield$_{VA}$	% CE$_{VA}$	% CE$_{total}$
20°C	1	1.10	13.41	0.18	1.11	0.88	11.70	0.13	0.77	0.35	19.15	26.33
	2	3.65	1.93	0.12	0.39	0.23	7.97	0.31	0.93	0.83	31.98	39.92
	3	3.66	12.46	0.08	0.16	0.11	4.17	0.18	0.34	0.30	13.99	18.17
	4	4.10	11.66	0.15	0.22	0.19	5.00	0.24	0.35	0.41	14.67	19.66
	5	6.94	8.53	0.20	0.23	0.30	5.71	0.34	0.38	0.75	17.57	23.28
	6	9.44	6.72	0.21	0.19	0.16	5.88	0.38	0.34	0.83	17.60	23.48
50°C	1	13.54	4.99	0.16	1.00	0.55	35.94	0.32	1.95	1.41	29.73	19.97
	2	22.57	9.34	0.43	1.28	1.29	8.64	0.51	1.53	2.04	10.39	3.95
	3	22.35	10.56	0.41	0.81	0.94	3.02	0.48	0.94	1.76	7.59	5.55
	4	24.04	6.68	0.62	0.88	1.93	2.77	0.64	0.92	2.52	10.53	13.25
	5	28.89	8.90	0.58	0.65	1.65	1.64	0.59	0.66	2.30	7.06	8.67
	6	32.88	10.55	0.70	0.64	2.05	1.94	0.65	0.60	2.53	6.47	8.39

Table SI 2. Performance parameters for the ECH of 10 mM levulinic acid at different potentials at 50°C for 4-h electrolysis at 300 rpm. WE: Pt/Pt, CE: Pt, RE: Ag/AgCl (sat'd KCl). n=3

MEAN	ΔQ	$C_{balance}$ %	$c_{\gamma\text{-VL}}$ mM	Product formation rate$_{\gamma\text{-VL}}$ µmol h^{-1} cm^{-2}	% Yield$_{\gamma\text{-VL}}$	% CE$_{\gamma\text{-VL}}$	c_{VA} mM	Product formation rate$_{VA}$ µmol h^{-1} cm^{-2}	% Yield$_{VA}$	% CE$_{VA}$	% CE$_{total}$
−0.085 V	243.17	84.90	0.88	5.39	4.56	3.61	0.15	0.93	0.86	1.40	5.00
0.015 V	19.42	107.17	0.62	3.77	3.15	49.19	0.43	2.63	2.05	60.48	76.34
0.065 V	14.57	91.85	0.11	0.70	0.57	7.44	0.30	1.81	0.47	38.15	45.59
0.115 V	7.43	93.90	0.03	0.20	0.13	3.47	0.17	1.00	0.54	44.49	47.96
STD DEV	ΔQ	$C_{balance}$ %	$c_{\gamma\text{-VL}}$ mM	Product formation rate$_{\gamma\text{-VL}}$ µmol h^{-1} cm^{-2}	% Yield$_{\gamma\text{-VL}}$	% CE$_{\gamma\text{-VL}}$	c_{VA} mM	Product formation rate$_{VA}$ µmol h^{-1} cm^{-2}	% Yield$_{VA}$	% CE$_{VA}$	% CE$_{total}$
−0.085 V	53.93	13.03	0.25	1.53	0.54	1.34	0.08	0.48	0.45	1.01	2.20
0.015 V	13.54	4.99	0.16	1.00	0.55	35.94	0.32	1.95	1.41	29.73	19.97
0.065 V	0.33	11.31	0.03	0.17	0.17	1.80	0.10	0.61	0.64	11.99	13.22
0.115 V	1.14	9.69	0.05	0.28	0.19	4.91	0.11	0.63	0.31	27.78	22.97

Table SI 3. Performance parameters for the ECH of 100 mM levulinic acid at 50°C for 4-h electrolysis at 300 rpm. E_{app}=+0.015 V vs RHE. WE: Pt/Pt, CE: Pt, RE: Ag/AgCl (sat'd KCl). n=3

MEAN	time	ΔQ	$C_{balance}$ %	$c_{\gamma\text{-VL}}$ mM	Product formation rate$_{\gamma\text{-VL}}$ µmol h^{-1} cm^{-2}	% Yield$_{\gamma\text{-VL}}$	% CE$_{\gamma\text{-VL}}$	c_{VA} mM	Product formation rate$_{VA}$ µmol h^{-1} cm^{-2}	% Yield$_{VA}$	% CE$_{VA}$	% CE$_{total}$
100 mM	1	60.33	95.40	1.78	10.91	1.50	27.23	1.45	8.88	1.22	44.56	71.79
	2	93.33	96.21	2.68	8.03	2.25	26.13	1.93	5.80	1.62	37.98	64.12
	3	125.73	93.93	3.66	7.16	3.01	26.17	2.47	4.83	2.03	34.79	60.97
	4	162.40	95.48	4.46	6.42	3.75	24.13	2.87	4.12	2.41	30.70	54.83
STD DEV	time	ΔQ	$C_{balance}$ %	$c_{\gamma\text{-VL}}$ mM	Product formation rate$_{\gamma\text{-VL}}$ µmol h^{-1} cm^{-2}	% Yield$_{\gamma\text{-VL}}$	% CE$_{\gamma\text{-VL}}$	c_{VA} mM	Product formation rate$_{VA}$ µmol h^{-1} cm^{-2}	% Yield$_{VA}$	% CE$_{VA}$	% CE$_{total}$
100 mM	1	5.44	2.25	0.21	1.27	0.17	1.34	0.22	1.34	0.17	6.74	5.76
	2	6.85	0.56	0.26	0.78	0.21	0.93	0.38	1.15	0.30	8.04	7.45
	3	13.34	0.50	0.26	0.51	0.17	0.97	0.63	1.23	0.50	6.73	5.76
	4	12.33	0.94	0.50	0.72	0.37	1.40	0.81	1.16	0.65	7.11	7.74

Table SI 4. Performance parameters for the ECH of 10 mM furfural at different applied potentials at 20°C for 1-h electrolysis at 300 rpm. WE: Pt/Pt, CE: Pt, RE: Ag/AgCl (sat'd KCl). n=3

MEAN	ΔQ C	$C_{balance}$ %	c_{FA} mM	n_{FA} mmol	Y_{FA} %	CE_{FA} %	c_{MF} mM	n_{MF} mmol	Y_{MF} %	CE_{MF} %	c_{Furan} mM	n_{Furan} mmol	Y_{Furan} %	CE_{Furan} %	CE_{total} %
0.165 V	12.68	74.44	0.01	0.00	0.08	0.98	0.09	LOD	0.60	16.35	LOD	LOD	0.02	0.15	17.33
0.115 V	12.53	85.12	0.01	0.00	0.09	1.54	0.13	0.01	1.12	29.06	0.02	LOD	0.15	1.16	30.61
0.065 V	19.28	85.46	0.16	0.01	1.22	9.46	0.15	0.01	1.26	17.80	0.01	LOD	0.09	0.29	27.26
0.015 V	26.50	84.08	0.18	0.01	1.64	6.98	0.33	0.02	2.80	24.92	LOD	LOD	0.03	0.08	31.90
−0.085 V	123.24	75.17	0.61	0.03	5.05	4.61	0.38	0.02	2.96	5.42	0.02	LOD	0.13	0.06	10.03
STD DEV	ΔQ C	$C_{balance}$ %	c_{FA} mM	n_{FA} mmol	Y_{FA} %	CE_{FA} %	c_{MF} mM	n_{MF} mmol	Y_{MF} %	CE_{MF} %	c_{Furan} mM	n_{Furan} mmol	Y_{Furan} %	CE_{Furan} %	CE_{total} %
0.165 V	4.87	6.82	0.02	0.00	0.12	1.38	0.07	0.00	0.54	12.80	0.00	0.00	0.01	0.09	14.18
0.115 V	6.23	8.95	0.01	0.00	0.09	1.54	0.05	0.00	0.31	21.03	0.01	0.00	0.11	1.07	22.58
0.065 V	9.88	8.41	0.07	0.00	0.56	6.33	0.21	0.01	1.86	21.55	0.02	0.00	0.15	0.40	27.88
0.015 V	8.73	12.24	0.02	0.00	0.33	1.89	0.07	0.00	0.54	8.84	0.00	0.00	0.02	0.05	10.73
−0.085 V	3.24	13.38	0.12	0.01	1.13	1.02	0.28	0.01	2.18	4.00	0.01	0.00	0.11	0.05	5.02

Table SI 5. Performance parameters for the ECH of furfural at different concentrations at 20°C for 1-h electrolysis at 300 rpm. E_{app}=+0.015 V vs RHE. WE: Pt/Pt, CE: Pt, RE: Ag/AgCl (sat'd KCl). n=3

MEAN	ΔQ C	$C_{balance}$ %	c_{FA} mM	Product formation rate$_{FA}$ µmol h^{-1} cm^{-2}	Y_{FA} %	CE_{FA} %	c_{MF} mM	Product formation rate$_{MF}$ µmol h^{-1} cm^{-2}	Y_{MF} %	CE_{MF} %	c_{Furan} mM	Product formation rate$_{Furan}$ µmol h^{-1} cm^{-2}	Y_{Furan} %	CE_{Furan} %	CE_{total} %
1 mM	27.37	46.85	0.09	0.54	5.58	2.68	0.08	0.45	6.55	5.23	LOD	0.01	0.16	0.02	7.91
2.5 mM	30.47	78.70	0.21	1.29	8.15	6.35	0.17	1.03	6.59	12.50	LOD	0.01	0.09	0.07	18.84
5 mM	28.10	91.70	0.24	1.44	4.35	8.10	0.32	1.93	5.76	23.00	LOD	0.02	0.05	0.12	31.11
10 mM	23.53	82.59	0.18	1.07	1.55	7.61	0.36	2.09	2.99	29.29	LOD	0.02	0.03	0.09	36.90
25 mM	24.13	97.95	0.40	2.47	1.70	14.92	0.41	2.50	1.74	32.15	LOD	0.02	0.02	0.19	47.07
50 mM	25.27	97.88	0.34	2.08	0.65	12.86	0.42	2.88	0.92	35.32	0.01	0.04	0.01	0.19	48.18
STD DEV	ΔQ C	$C_{balance}$ %	c_{FA} mM	Product formation rate$_{FA}$ µmol h^{-1} cm^{-2}	Y_{FA} %	CE_{FA} %	c_{MF} mM	Product formationrate$_{MF}$µmol h^{-1} cm^{-2}	Y_{MF} %	CE_{MF} %	c_{Furan} mM	Product formation rate$_{Furan}$ µmol h^{-1} cm^{-2}	Y_{Furan} %	CE_{Furan} %	CE_{total} %
1 mM	3.11	20.36	0.12	0.71	6.57	3.44	0.06	0.33	5.80	4.11	0.00	0.00	0.07	0.00	7.55
2.5 mM	7.69	6.52	0.08	0.47	3.06	1.24	0.07	0.40	2.73	8.28	0.00	0.00	0.02	0.00	9.52
5 mM	8.75	2.35	0.06	0.36	1.26	1.14	0.02	0.14	0.76	5.79	0.00	0.01	0.02	0.00	6.93
10 mM	8.15	13.81	0.02	0.13	0.34	1.77	0.05	0.29	0.49	5.29	0.00	0.01	0.02	0.05	7.07
25 mM	5.09	1.72	0.21	1.28	0.83	6.21	0.17	1.05	0.47	10.33	0.00	0.01	0.01	0.00	16.54
50 mM	6.86	2.01	0.11	0.67	0.17	3.31	0.12	0.76	0.29	1.15	0.00	0.00	0.00	0.00	4.46

Table SI 6. Performance parameters for the ECH of furfural and levulinic acid of selected literature studies.

Catalyst	$E_{app, RHE}$	Substrate	Electrolyte*	Production rate 2H-P	Production rate 4H-P	CE_{total} %
Cu[1]	-0.55 V[a]	50 mM FF	75:25 0.5 M H_2SO_4:ACN	13.0 µmol h^{-1} cm^{-2}	80.0 µmol h^{-1} cm^{-2}	70%
Cu[2]	-0.56 V	10 mM FF	80:20 0.1 M H_2SO_4:ACN	12.47 µmol h^{-1} cm^{-2}	16.80 µmol h^{-1} cm^{-2}	21%
Pd/C[3]	-0.1 V	50 mM FF	0.1 $HClO_4$	2.05 µmol h^{-1} cm^{-2}	n.d.	97%
	-0.2 V	50 mM FF	0.1 $HClO_4$	3.6 µmol h^{-1} cm^{-2}	n.d.	91%
Pt on Pd/Pd[4]	-75 mA	0.25 M FF	t-BuOH/1 M H_2SO_4	2.67 µmol h^{-1} cm^{-2}	n.d.	n.d.
Pb[5]	-1.3 V	0.20 M LA	0.5 M H_2SO_4	17.5 µmol h^{-1} cm^{-2}	244.0 µmol h^{-1} cm^{-2}	87%
	-1.5 V	0.20 M LA	0.5 M H_2SO_4	13.3 µmol h^{-1} cm^{-2}	417.42 µmol h^{-1} cm^{-2}	92%
5-In/CF[6]	-1.3 V	50 mM LA	0.1 M H_2SO_4	3.13 mmol h^{-1} cm^{-2} mg cat.	33.48 mmol h^{-1} cm^{-2} mg cat.	37.1%

*at room temperature; n.d. - not determined

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