Energy demand of electrochemical FA production

Table S1: Energy demand for the production of formic acid for different voltages and faradic efficiencies in kJ mol^{-1}

Faradic efficiency → Voltage / V ↓	50%	60%	70%	80%	90%	95%	100%
1	385.9	321.6	275.7	241.2	214.4	203.1	193.0
1.5	578.9	482.4	413.5	361.8	321.6	304.7	289.5
1.7	656.1	546.8	468.6	410.1	364.5	345.3	328.1
1.8	694.7	578.9	496.2	434.2	385.9	365.6	347.3
1.9	733.3	611.1	523.8	458.3	407.4	385.9	366.6
2	771.9	643.2	551.3	482.4	428.8	406.3	385.9
2.1	810.5	675.4	578.9	506.5	450.3	426.6	405.2
2.2	849.1	707.6	606.5	530.7	471.7	446.9	424.5
2.3	887.7	739.7	634.0	554.8	493.1	467.2	443.8
2.4	926.3	771.9	661.6	578.9	514.6	487.5	463.1
2.5	964.9	804.0	689.2	603.0	536.0	507.8	482.4
2.6	1003.4	836.2	716.7	627.2	557.5	528.1	501.7
2.7	1042.0	868.4	744.3	651.3	578.9	548.4	521.0
2.75	1061.3	884.4	758.1	663.3	589.6	558.6	530.7

Table S2: Energetic efficiency for the production of formic acid for different voltages and faradic efficiencies in %

Faradic efficiency → Voltage / V ↓	50%	60%	70%	80%	90%	95%	100%
1	62.7	75.2	87.7	100.3	112.8	119.1	125.4
1.5	41.8	50.1	58.5	66.9	75.2	79.4	83.6
1.7	36.9	44.2	51.6	59.0	66.4	70.1	73.7
1.8	34.8	41.8	48.7	55.7	62.7	66.2	69.6
1.9	33.0	39.6	46.2	52.8	59.4	62.7	66.0
2	31.3	37.6	43.9	50.1	56.4	59.5	62.7
2.1	29.8	35.8	41.8	47.8	53.7	56.7	59.7
2.2	28.5	34.2	39.9	45.6	51.3	54.1	57.0
2.3	27.3	32.7	38.2	43.6	49.1	51.8	54.5
2.4	26.1	31.3	36.6	41.8	47.0	49.6	52.2
2.5	25.1	30.1	35.1	40.1	45.1	47.6	50.1
2.6	24.1	28.9	33.7	38.6	43.4	45.8	48.2
2.7	23.2	27.9	32.5	37.1	41.8	44.1	46.4
2.75	22.8	27.4	31.9	36.5	41.0	43.3	45.6

Neglected energy demands: heat losses to ambience, energy demand for provision of CO_2.

Energy demand for the bicarbonate / formate approach

Table S3. Assumptions made for estimating energy demand of the bicarbonate / formate approach

Concentration of formate / bicarbonate	5 ± 1 M	based on Bi et al., 2014 [1]
Ambient temperature	20 °C	
Reaction temperature - charging	40 ± 5 °C	based on Bi et al., 2014 [1]
Charging pressure	40 ± 5 bar	based on Bi et al., 2014 [1]
Efficiency of compressor	60 ± 5 %	
Conversion in hydrogenation reaction	100 %	*Estimate*
Reaction temperature - discharging	80 ± 5 °C	based on Papp et al, 2011 [2]
Discharging pressure	6 bar	based on Papp et al, 2011 [2]
Conversion in dehydrogenation reaction	100 %	*Estimate*

Assumptions for internal heat recovery:
  o During charging: 50 % of the heat released during H_2 compression can be used for preheating
  o During discharging: the hot bicarbonate solution is used to preheat the cold formate solution entering the reactor; 20 K temperature that cannot be covered by internal heat integration		

Neglected energy demands: heat losses to ambience and energy demand for mixing and gas introduction.

Energy demand for catalytic decomposition of FA to H_2 and CO_2

Table S4. Assumptions made for estimating energy demand for catalytic hydrogen release from FA

Concentration of formate / bicarbonate	4 ± 2 M	based on Fellay et al., 2008 [3]
Ambient temperature	20 °C	
Reaction temperature	80 ± 20 °C	based on Fellay et al., 2008 [3]
Share of water / formic acid evaporated	10 ± 5 % 5 ± 2.5 %	*Estimate*
conversion	100%	*Estimate*

Assumptions for internal heat recovery:
  o Cold FA solution is preheated by cooling the hot streams leaving the reactor
  o It is assumed that 20 ± 10 K of the temperature difference must be provided externally, because of limitations in heat transfer		

Neglected energy demands: heat losses to ambience.

Energy demand for thermal decomposition of FA to H_2O and CO

Table S5. Assumptions made for estimating energy demand for thermal carbon monoxiderelease from FA

Ambient temperature	20 °C	
Reaction temperature	500 ± 100 °C	Estimate based on Blake et al., 1971 [4]
conversion	100%	*Estimate*

Assumptions for internal heat recovery:
  o Cold FA is preheated by cooling the hot stream leaving the reactor
  o It is assumed that 100 ± 25 K of the temperature difference must be provided externally, because of limitations in heat transfer		

Neglected energy demands: heat losses to ambience.

Data on direct formic acid fuel cells

Table S6: Crossover current data reported by Jeong et al.[5] at 30 °C for a direct formic acid fuel cell membrane

c(FA)	no electric current		electric current $j = 90$ mA cm^{-2}			electric current $j = 137$ mA cm^{-2}		
	Crossover current	molar Flux	Crossover current	molar Flux	loss due to crossover	Crossover current	molar Flux	loss due to crossover
mol L^{-1}	mA cm^{-2}	mol cm^{-2} s^{-1}	mA cm^{-2}	mol cm^{-2} s^{-1}	%	mA cm^{-2}	mol cm^{-2} s^{-1}	%
2	20	1.0E-07						
6	29	1.5E-07	13	6.7E-08	12.6			
10	51	2.6E-07	33	1.7E-07	26.8	35	1.8E-07	20.3
12	63	3.3E-07	40	2.1E-07	30.8	50	2.6E-07	26.7
15	92	4.8E-07	60	3.1E-07	40.0	60	3.1E-07	30.5

Table S7: Voltages of direct formic acid fuel cell membranes at different current densities reported in literature

		Ha et al., 2004[6]			Rice et al., 2002 [7]	Larsen et al., 2006[8]		Ortiz-Ortega et al., 2014[9]		
		maximum	1.8M	1.8M	4.4M					
Current density	mA cm^{-2}	250	67	40	36		650	290	0	150	200
Power density	mW cm^{-2}	33	17.8	16	14.2		255	160	0	69	68
Voltage	V	0.13	0.27	0.40	0.39	0.72	0.39	0.55	0.89	0.46	0.34
Electric energy	kJ mol^{-1}	25.5	51.3	77.2	76.1	138.9	75.7	106.5	171.7	88.8	65.6
Efficiency	%	**10.5**	**21.2**	**31.9**	**31.5**	**57.4**	**31.3**	**44.0**	**71.0**	**36.7**	**27.1**

Neglected effects that might influence the efficiency of direct formic acid fuel cell:
- If the direct FAFC is fed with an aqueous solution of FA, the solvent water must be transported out of the cell to avoid its accumulation. This water will most likely transport a certain share of the FA out of the system.
- Ohmic losses
- Preheating (might be negligible, since the FAFC is operated near ambient temperature and the heat released by the cell seems to be sufficient).

Producing electricity from FA

Table S8: Assumptions made for estimating efficiency of electricity production from FA

All assumption concerning the individual release options as described in the respective tables above		
Provision of heat for decomposition	Partial combustion of hydrogen	
Energy demand for purification	21.7 kJ mol^{-1}	PSA; based on Liu et al., 2011[10]
Efficiency of fuel cell	60 ± 10 %	based on DoE report for status 2015[11]
Efficiency of ICE for repowering CO	37 ± 2 %	Based on Natkin et al., 2003[12]

Table S9: Energy demand for hydrogen release and efficiency for electricity production from FA assuming electric heating for heat provision to the release step

	energy demand / kJ mol^{-1}				$h_{FA \rightarrow Electricity}$ / % assuming electric heating; not considering purification			
	with heat recovery	±	without heat recovery	±	with heat recovery	±	without heat recovery	±
Catalytic (aqueous)	65.69	18.9	108.10	32.8	32.8	12.7	15.3	16.8
Catalytic (pure FA)	20.41	1.4	24.37	2.2	51.6	10.0	49.9	10.0
Bicarbonate	40.54	13.6	77.00	19.1	43.2	11.5	28.2	12.7
Biological	?	?	?	?	?	?	?	?
thermal	53.73	1.7	80.30	6.3	14.8	2.1	3.8	3.0
direct-FAFC	not applicable		not applicable				24	5

Table S10: Efficiency of electricity production from FA assuming partial combustion of hydrogen to cover the energy demand of the release step

	$h_{FA \rightarrow Electricity}$ / % assuming partial combustion of the gas; not considering purification				$h_{FA \rightarrow Electricity}$ / % assuming partial combustion of the gas; considering purification (PSA)			
	with heat recovery	±	without heat recovery	±	with heat recovery	±	without heat recovery	±
Catalytic (aqueous)	43.7	10.7	33.2	14.6	34.7	11.4	24.2	15.2
Catalytic (pure FA)	54.9	9.2	54.0	9.0	46.0	10.1	45.0	9.9
Bicarbonate	49.9	10.0	40.9	10.4	49.9	10.0	40.9	10.4
Biological	?	?	?	?	?	?	?	?
thermal	30.0	1.7	26.5	2.9	30.0	1.7	26.5	2.9
direct-FAFC			24	5			24	5

Sensitivity analysis: Bicarbonate / Formate approach
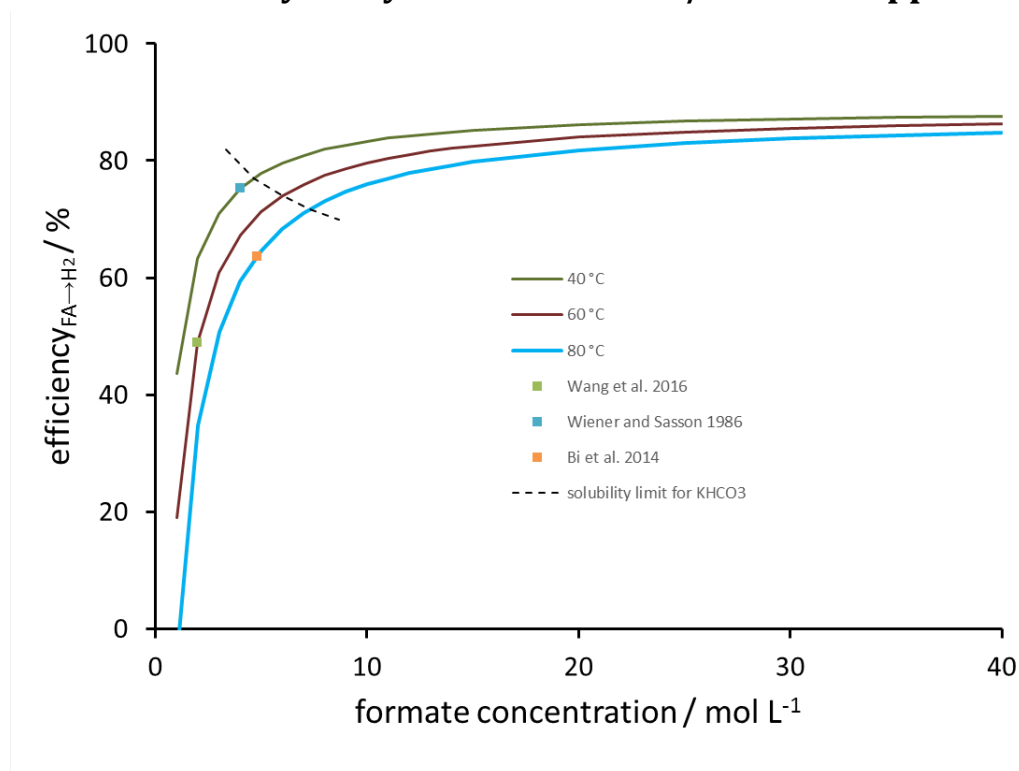

Figure S1: Efficiency of H$_2$ release from an aqueous solution of a formate salt as as a function of concentration for different temperatures; added are three examples for concentrations/temperatures found in literature and the solubility limit for potassium bicarbonate
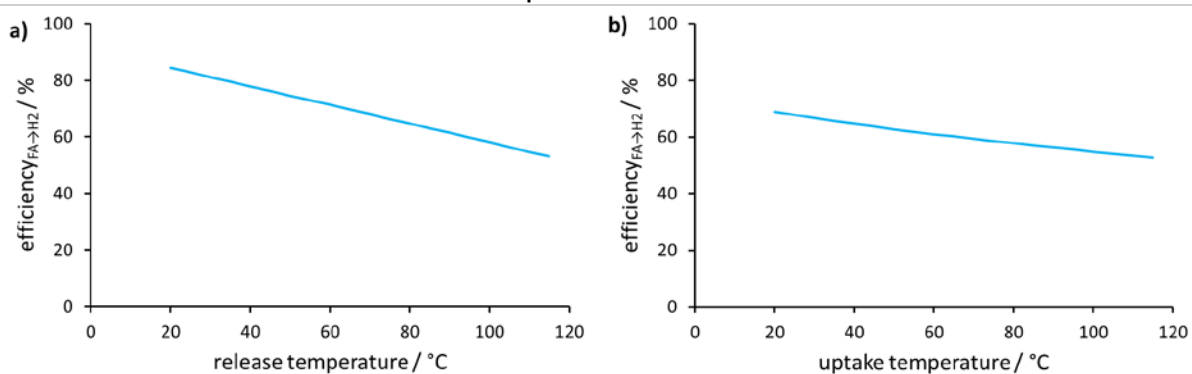

Figure S2: Efficiency of H$_2$ release from an aqueous solution of a formate salt as as a function of a) temperature of hydrogen release and b) temperature of hydrogen uptake
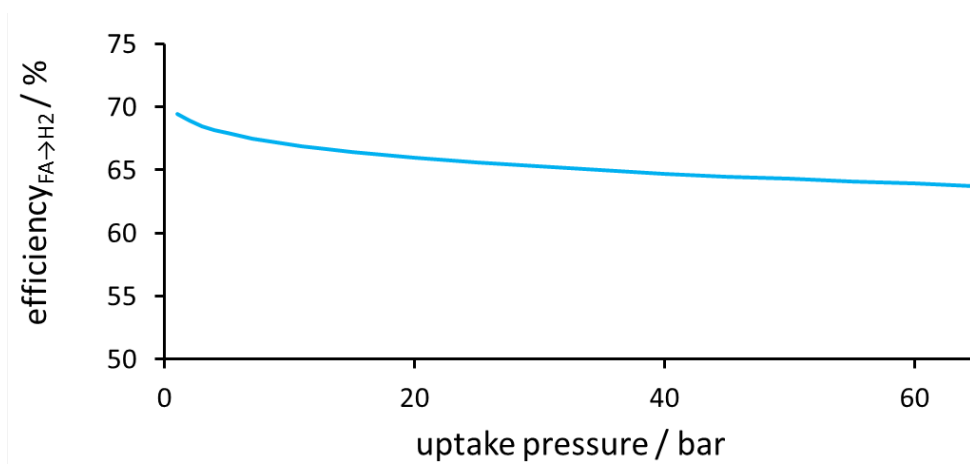
Figure S3 : Efficiency of H$_2$ release from an aqueous solution of a formate salt as a function of hydrogen pressure for the hydrogenation reaction of Bicarbonate to Formate

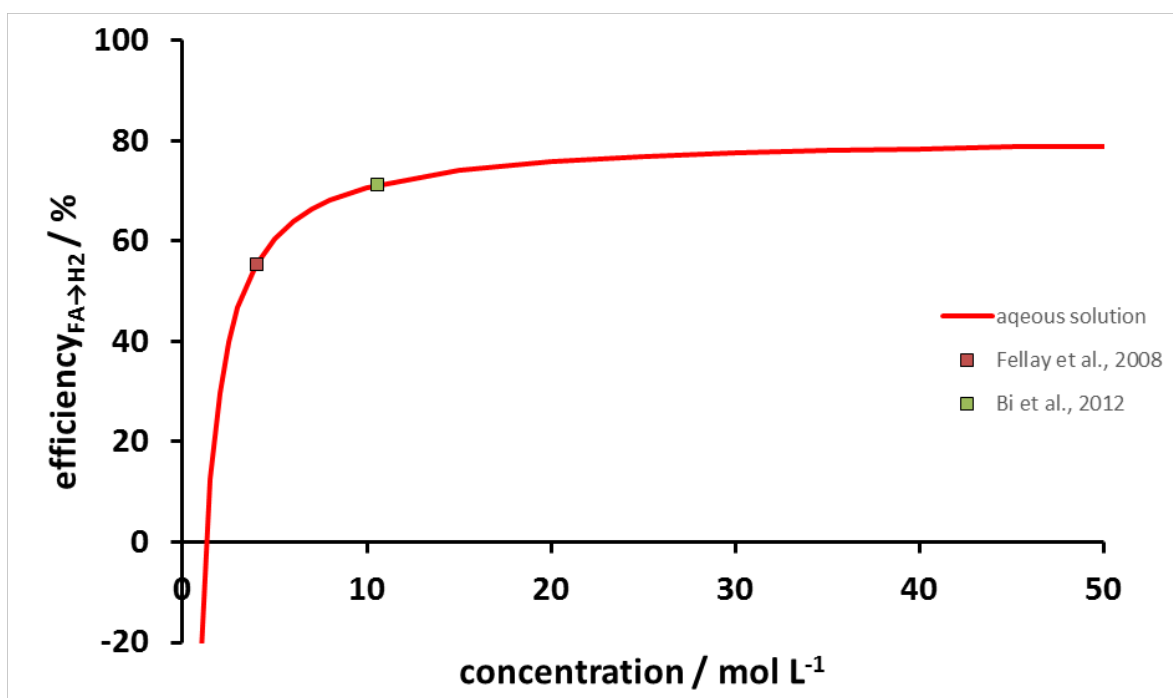# Sensitivity analysis: Catalytic decomposition of FA to H₂ and CO₂

Figure S4: Efficiency of catalytic H₂ release from FA at 80 °C as a function concentration; added are two examples for concentrations found in literature
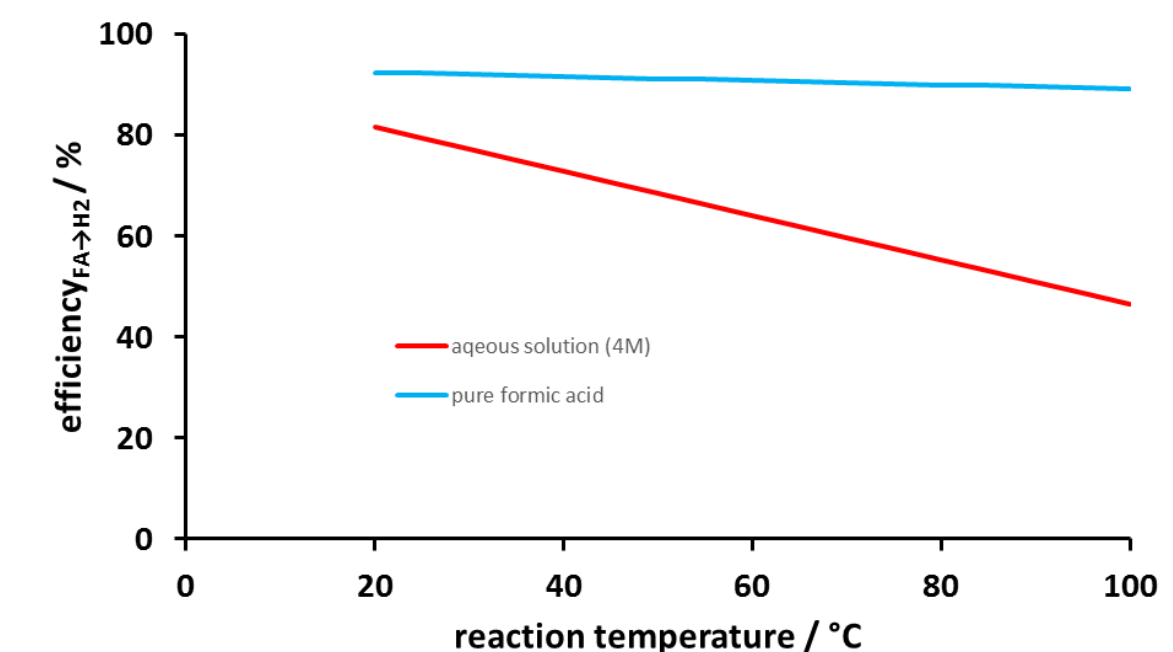

Figure S5: Efficiency of catalytic H₂ release from FC as function of reaction temperature

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