Supplementary information

Matching emerging formic acid synthesis processes with application requirements

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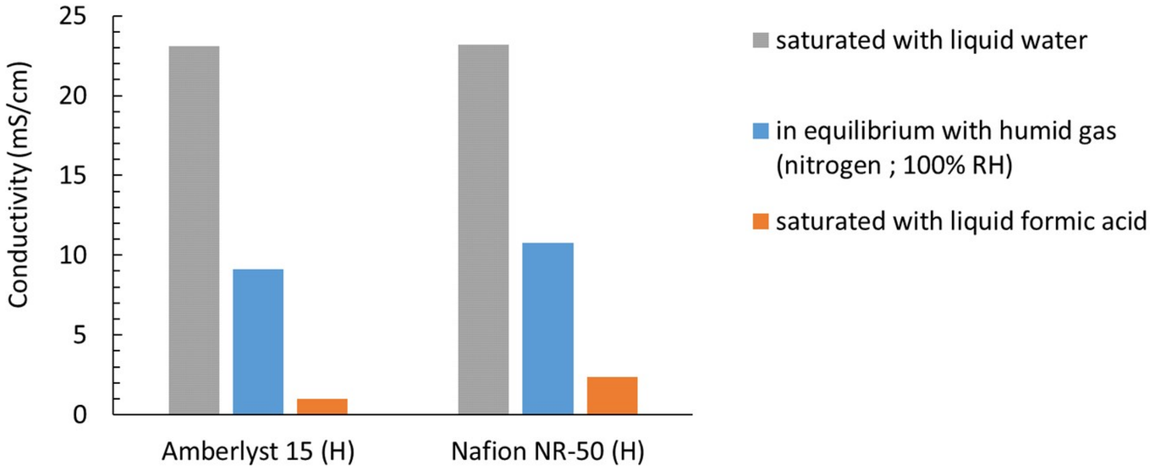


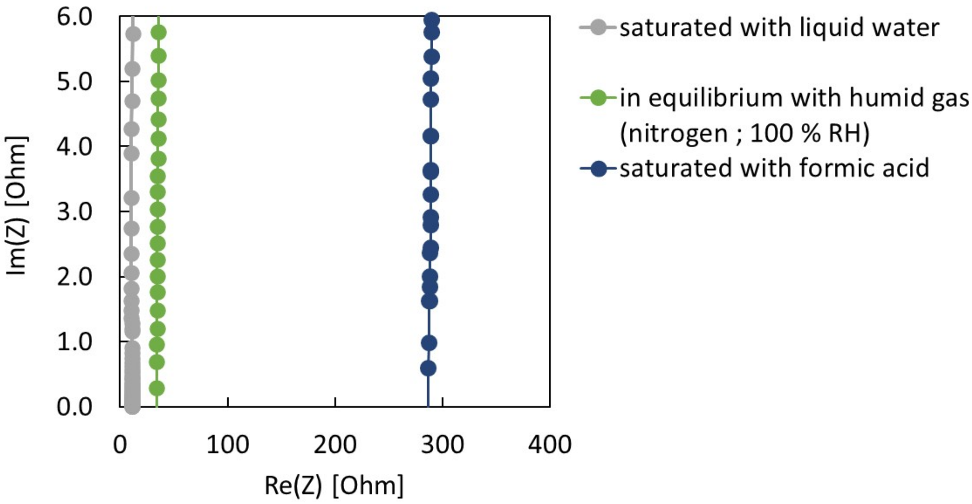
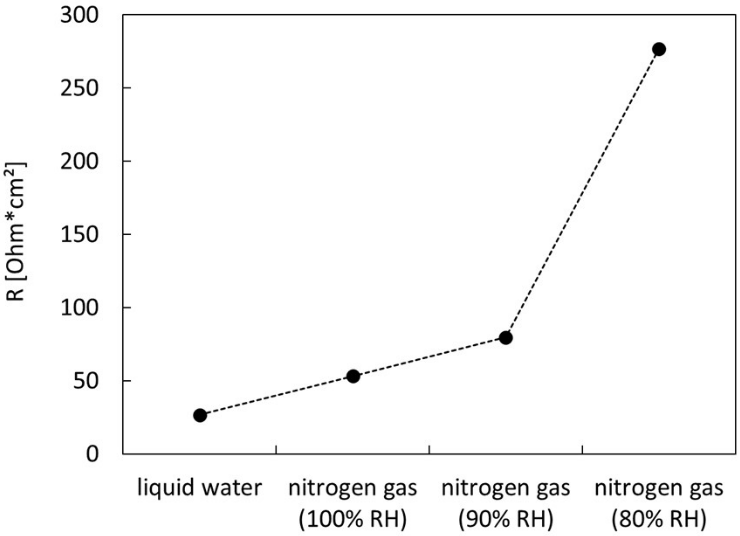


Fig. S1 : Top : Conductivity of two types of proton exchange solid state electrolyte ('PE-SSE') resin beads saturated either with liquid water, concentrated formic acid or after equilibration with a humid N_2 gas flow at a relative humidity of 100% at room temperature. A 5 mm thick layer of resin beads was pressed between two stainless steel plates and the resistance was determined from Nyquist plots obtained with potentiostatic electrochemical impedance spectroscopy (pEIS ; 0V). **Bottom :** Nyquist plots for Amberlyst 15 (H) PE-SSE resin beads.



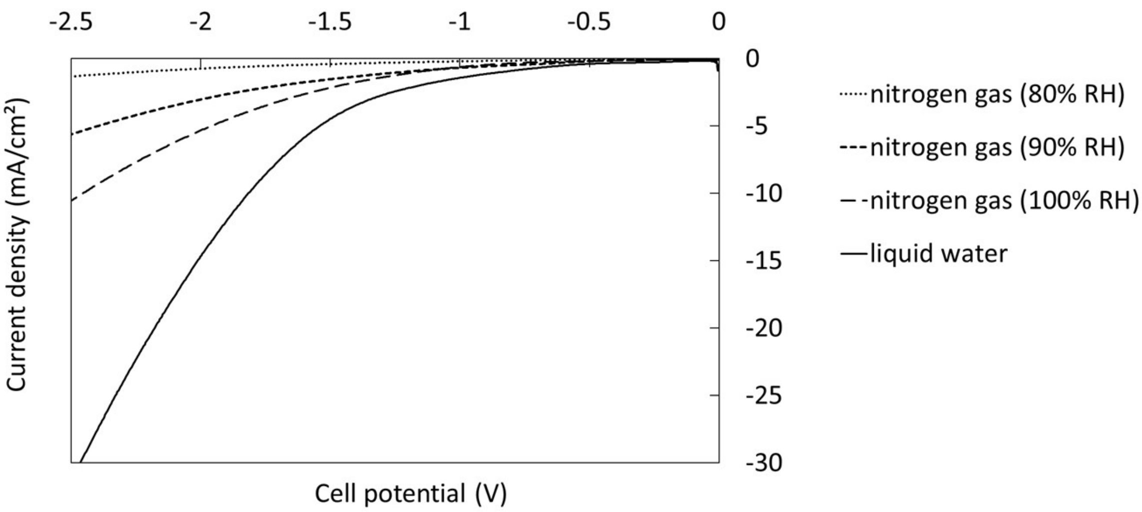


Fig. S2 : Resistance measurements (**top**) and cyclic voltammetry (CV) measurements (**bottom**) for a three-compartment electrolyser for CO_2 reduction to formic acid at different humidity conditions. The membrane electrode assembly consisted of a Pt on C-cloth anode, a PEM (Nafion 117), SSE resin (Amberlyst-15H ; 3 mm thick layer), AEM (Fumasep FAD-PET-75) and Sn/Cu cathode coated with Pention D35 ionomer. In the middle compartment, either a liquid water flow or a humid gas flow was used. **Top** : The resistance was measured with potentiostatic electrochemical impedance spectroscopy (pEIS ; 0V) after exposing the MEA to the operating conditions until an equilibrium value was reached for the resistance, which is depicted here. **Bottom** : The CV curves were measured at equilibrium at a scan rate of 5 mV/s.

Table S1 : additional information for the determination of the round-trip efficiencies for various energy storage media. Transport is not taken into account.

	Li-ion battery	**Pumped hydro**	**Hydrogen *1**		**Methane *2**	**Ammonia *3**	**Formic acid *4**
			Compressed (350 - 700 bar)	Liquefied	Compressed	Liquefied	
Energy to fuel (kWh/kg)			50 – 55				2.6 - 5.7
Fuel processing (kWh/kg)			2 – 6	7 - 13			2.3 – 9.6
Energy content (LHV)			33.3			5.2	1.72
Conversion efficiency (%)			55 - 64	49 - 58		43 - 52	11 - 35
Reconversion efficiency (%)			50 - 70			45	45
Round-trip efficiency (%)	**80 – 95**	**70 – 80**	**34 - 45**	**25 - 41**	**30 - 38**	**19 - 23**	**5 - 16**

***1 : Hydrogen**

Assuming H_2 formation from renewable energy with a PEM electrolyser with an energy efficiency of ca.70%,[1] followed by compression or liquefaction[2] and reconversion to energy in a hydrogen fuel cell with an energy efficiency of 50-70%.[3]

***2 : Methane**

Assuming H_2 formation from renewable energy by an electrolyser, catalytic CO_2 methanation by the Sabatier-Senderens reaction and compression to 80 bar.[4]

***3 : Ammonia**

Assuming one kg of ammonia production requires 9−15 kWh of energy.[5] For reconversion, ammonia is cracked into high-purity hydrogen, compressed and used in a PEMFC.[5]

***4 : Formic acid**

Assuming electrochemical production of formic acid from CO_2 and H_2O in a CO_2 electrolyzer. Post-processing is done by distillation and reconversion to energy by reforming of formic acid to H_2 followed by a H_2 fuel cell ("HYFORM-PEMFC", as described by Ma *et al.*[6]). Fuel processing of formic acid refers to the concentration process. A feed concentration of 10 wt.% is assumed, which requires 2.3-9.6 kWh/kg depending on the concentration method, as derived from Ramdin *et al.* (Fig. S4 from [7]), calculated from given operational cost in $/kg, assuming energy cost is biggest contributor to the operating costs with an electricity price of 50 $/MWh.[7]

References

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