Carbon negative H_2

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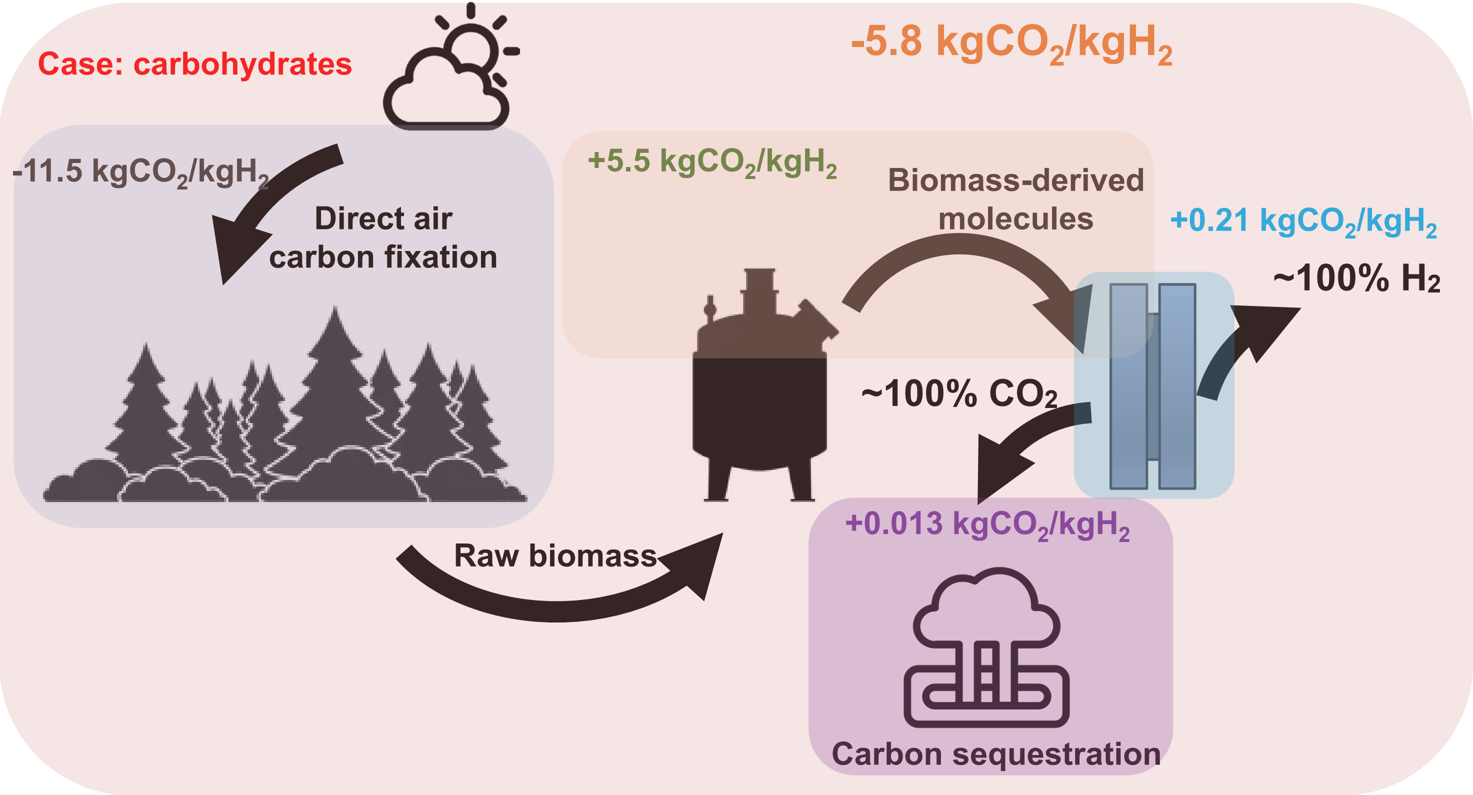
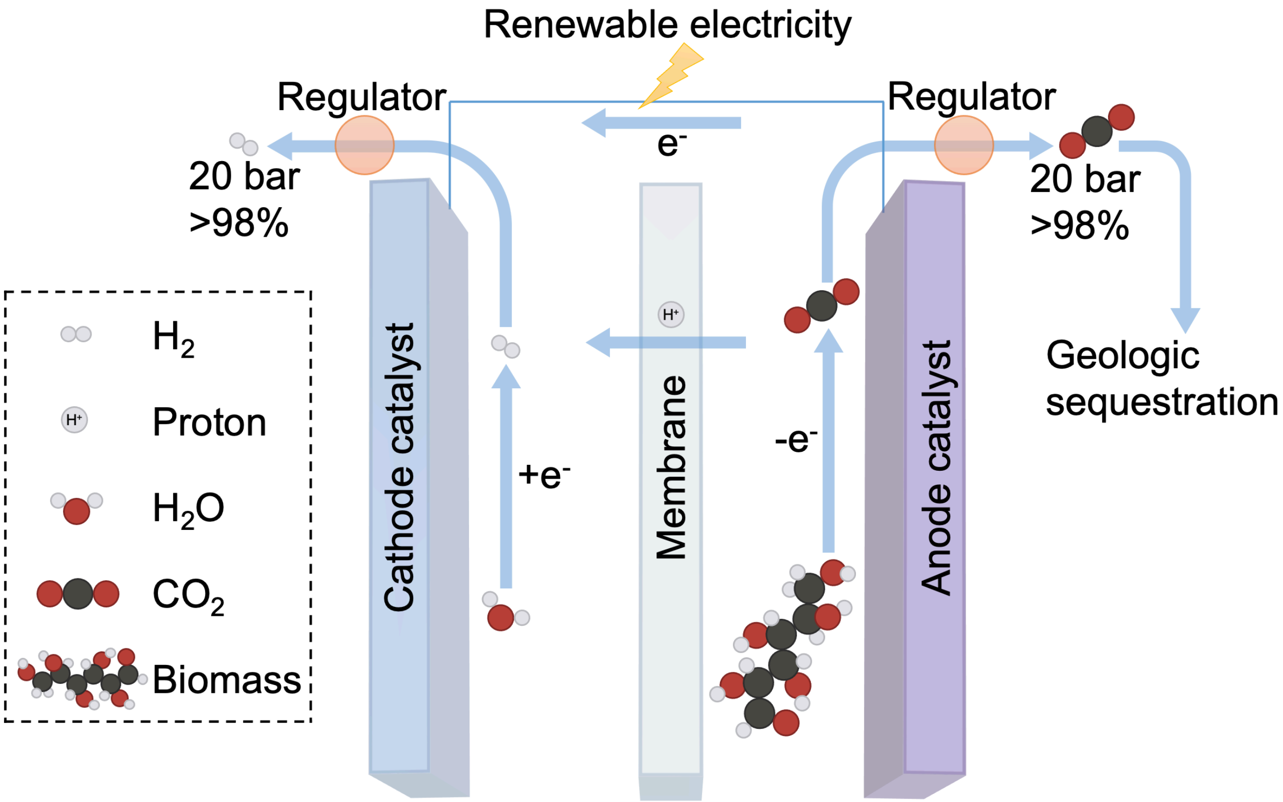
Low-energy-intensity electrified membrane separation splitting biomass into H_2 and CO_2 streams

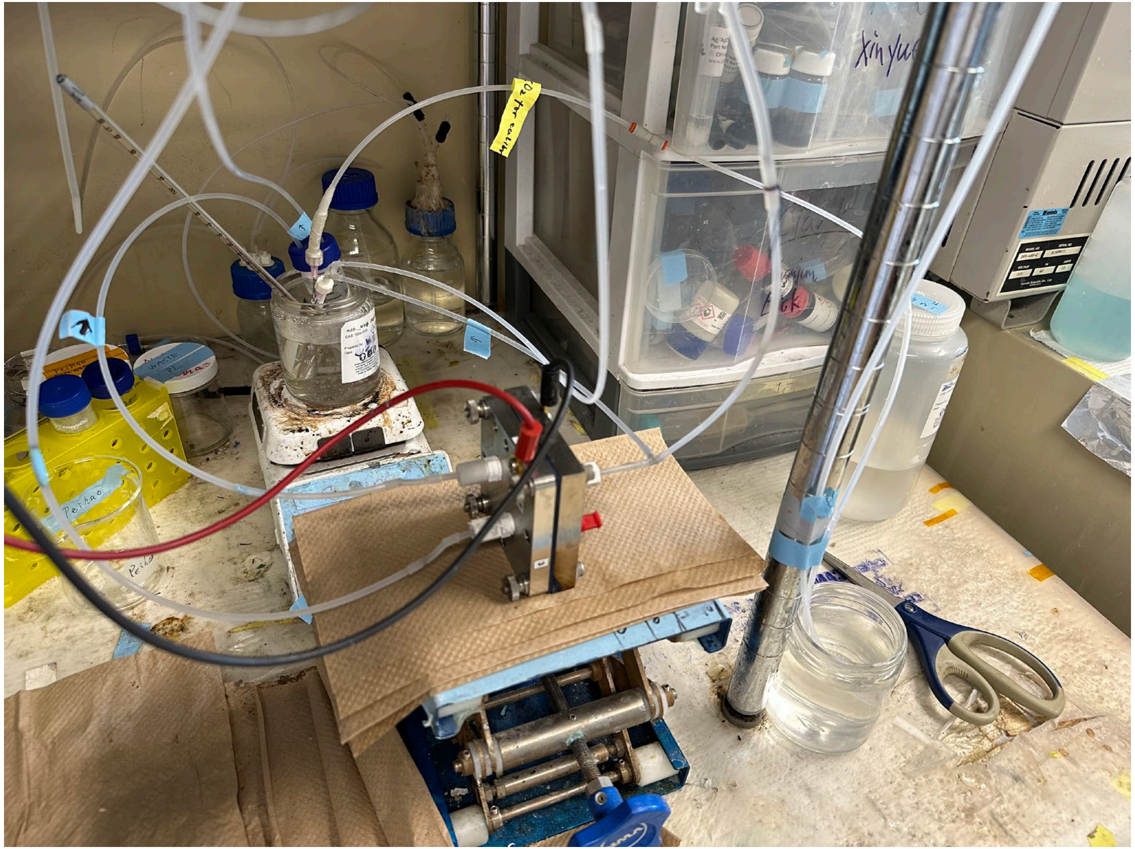
Splitting biomass into a pure H_2 stream and a pure CO_2 stream



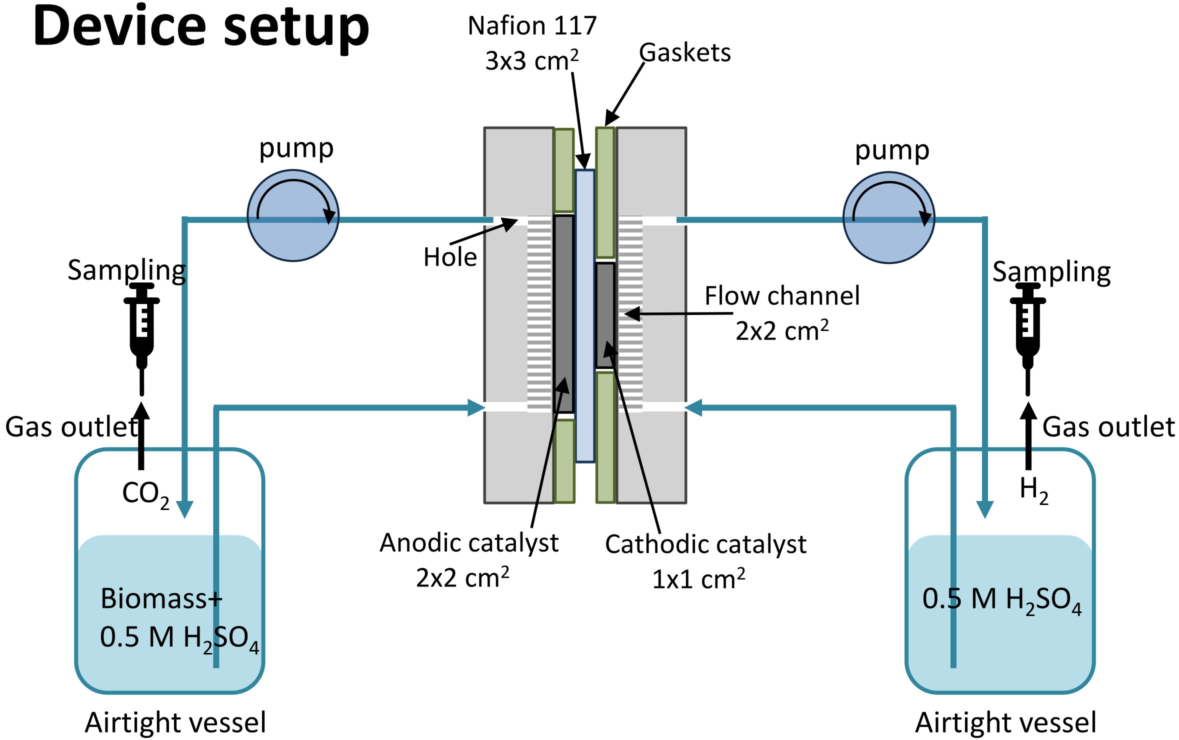
Concept schematic: biomass and electricity co-powered carbon-negative green H_2 production

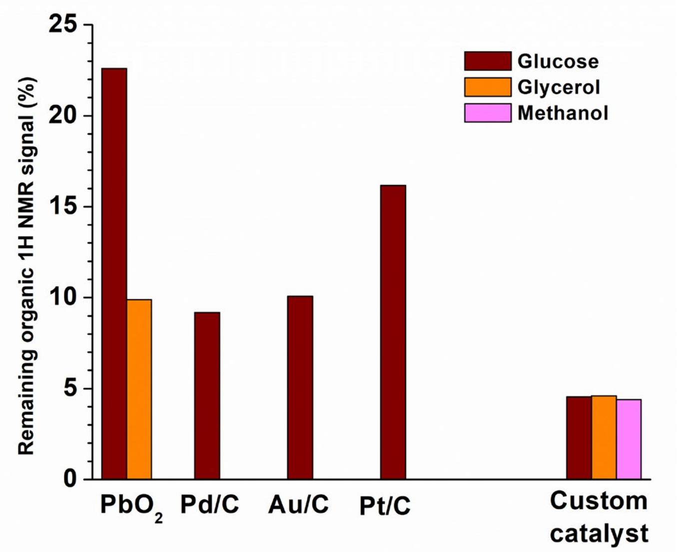


Photograph of devices reported on herein



Device setup



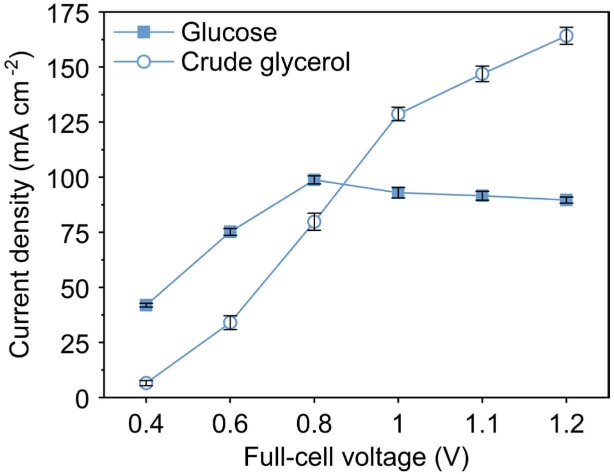


- Glucose electro-oxidation: $C_6H_{12}O_6 + 6H_2O - 24e^- = 6CO_2 + 24H^+$
- Glycerol electro-oxidation: $C_3H_8O_3 + 3H_2O - 14e^- = 3CO_2 + 14H^+$
- Methanol electro-oxidation: $CH_3OH + H_2O - 6e^- = CO_2 + 6H^+$
- ~20 h electrolysis to completely convert biomass to CO_2

- MEA electrolyzer
- Cathodic HER catalyst: Pt/C
- Anodic catalyst: custom catalyst, capable of converting biomass more completely

Electrochemical performance in crude glycerol, glucose, electrolysis

Current density vs. cell voltage

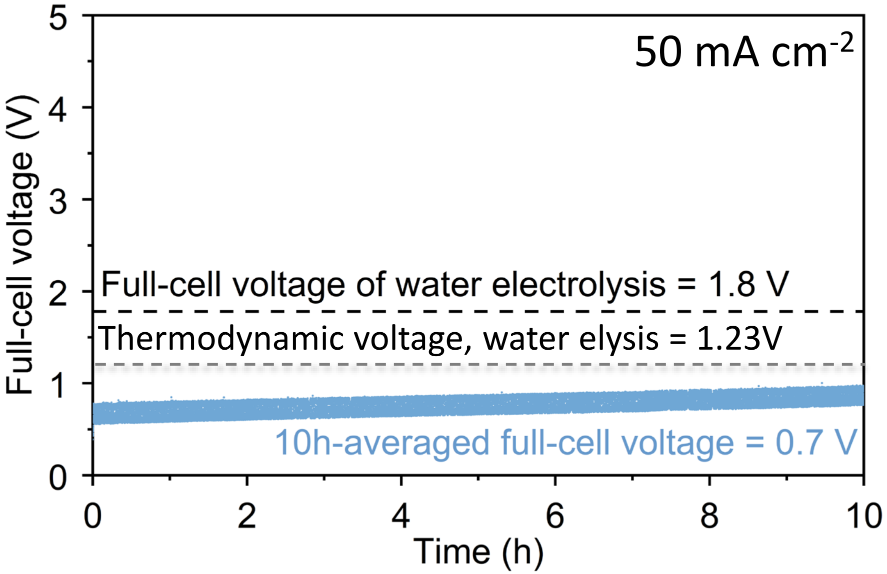


- Glycerol, methanol, and water were mixed to prepare lab-made crude glycerol, which was then dissolved in 0.5 mol L^{-1} H_2SO_4
- Next step: we will study the effect of salt in crude glycerol electrolysis. An example of alkaline crude glycerol contains sodium salt of fatty acid (0.5%–2% w/w), and sodium chloride (0.5%–2% w/w).[1]

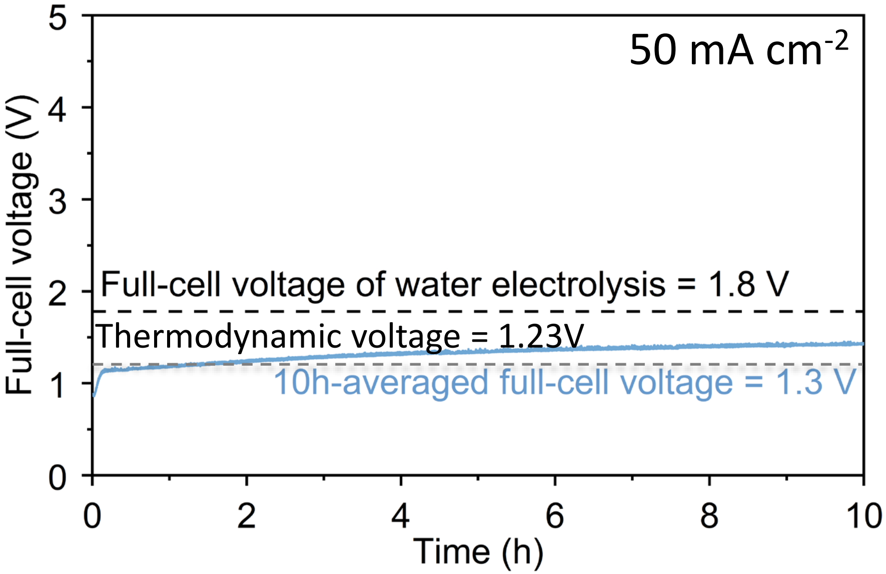
[1] Bioresource Technology 293 (2019) 122155

Crude glycerol, glucose electrolysis over 10h

Galvanostatic test of crude glycerol over 10h



Galvanostatic test of glucose over 10h



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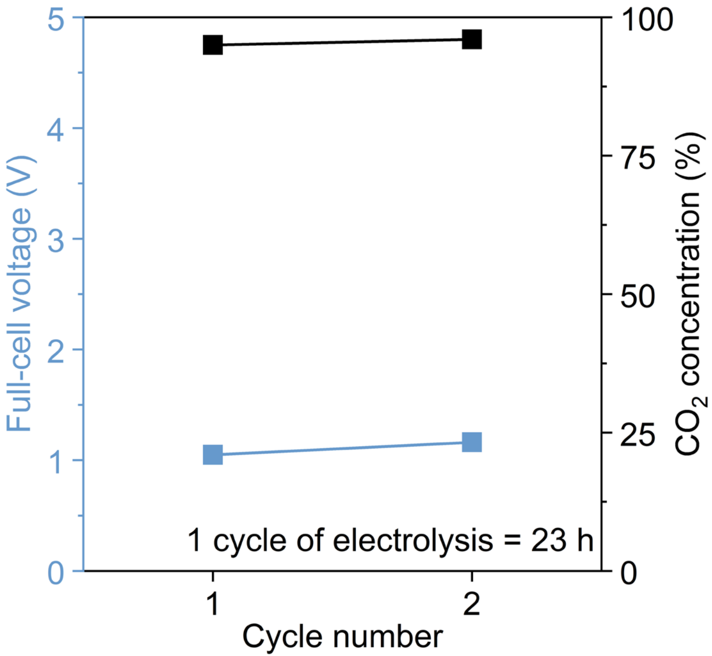
Anodic tail gas of crude glycerol, glucose electrolysis

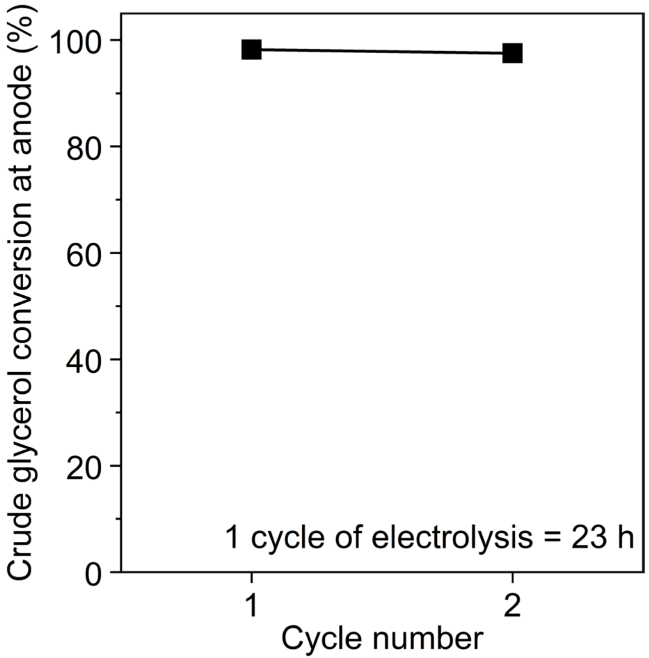
Anodic tail gas analysis (20-hours average)

	Crude glycerol	Glucose
CO_2	96%	93%
O_2	1%	2%
N_2	2%	2%
Ar	1%	3%

Note: The anolyte was purged with Ar, which came out with CO_2 in the tail gas. N_2 comes from system leakage to air. O_2 may be partially contributed by OER.

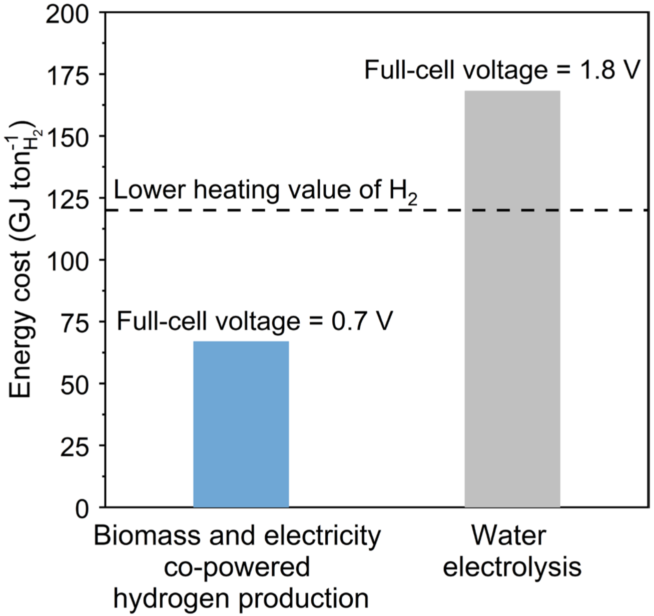
Membrane lifetime in crude glycerol electrolysis

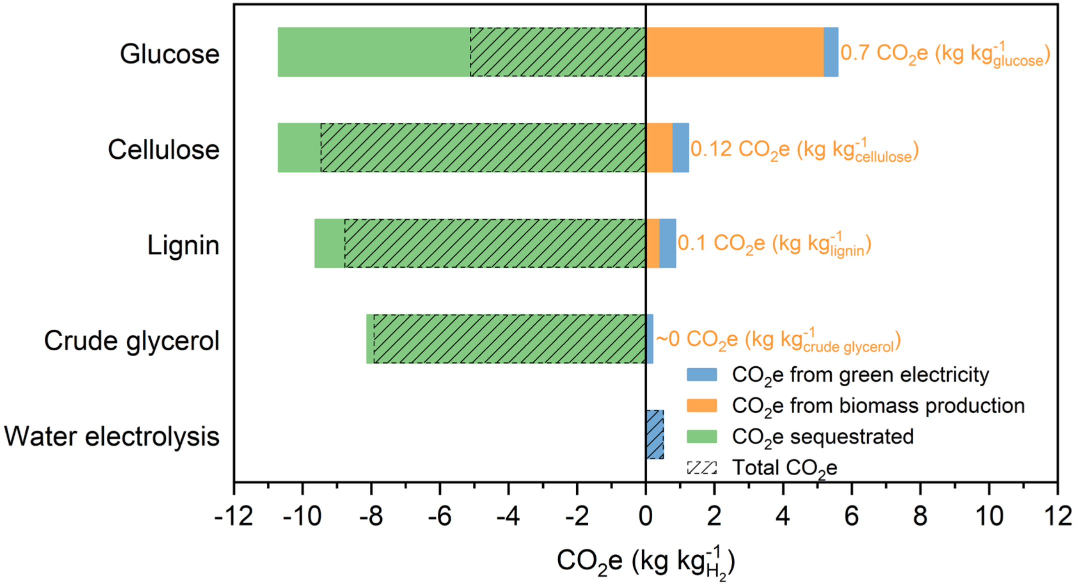




- Stable system performances over 2 cycles of electrolysis suggest no obvious evidence of membrane fouling
- Will try more cycles of electrolysis and examine membrane fouling

Energy cost and carbon intensity





- Carbon intensity of wind electricity: 11 CO_2 kWh^{-1}
- Full-cell voltages: glucose 1.3 V, cellulose & lignin 1.5 V, crude glycerol 0.7 V
- Biomass conversion = 98%

- Biomass electrolysis requires lower electricity than water electrolysis (1.76 V)
- The energy cost and carbon intensity of H_2-CO_2 separation is eliminated in our system
- High-purity CO_2 is geologically sequestrated to enable carbon-negative green H_2 production

Biomass carbon intensity references:
Glucose: *Journal of Cleaner Production 170 (2018) 610-624*
Cellulose: *Materials 2021, 14, 714*
Lignin: *Science of the Total Environment 770 (2021) 144656*

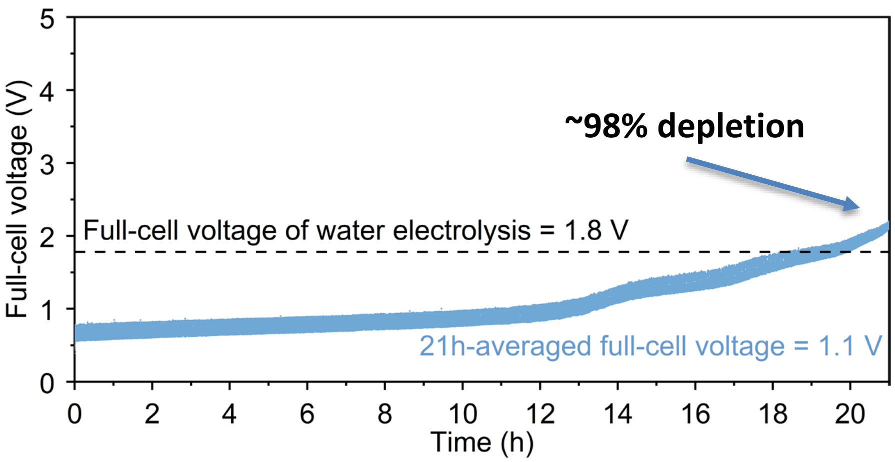
TEA and carbon intensity – rough estimates

	Blue H_2	Glucose H_2	Crude glycerol H_2
TEA (\$/kgH_2)			
Raw materials		2.06	0 (waste)
Process energy (\$0.03/kWh)		0.80 (assume 1.0 V)	0.56 (assume 0.7 V)
CAPEX		0.42	0.42
Plant-gate levelized cost \$/kg	**1.69-2.55**	**3.28**	**0.98**
Other revenue opportunity[a]		Credit \$0.35 if \$50/tonCO_2 Credit \$0.91 if \$100/tonCO_2	Credit \$0.25 if \$50/tonCO_2 Credit \$0.64 if \$100/tonCO_2
Carbon intensity (kgCO_2e/kgH_2)			
Raw materials preparation	6.0[b]	5.5[c]	0 (waste)
Process energy	1.6[b]	0.30[d]	0.21[d]
Carbon capture	1.8[b]	0.013[d] (compression)	0.009[d] (compression)
Total carbon footprint	**9.4**	**5.8**	**0.22**
Carbon footprint from air	N/A	-11.5	-8.1

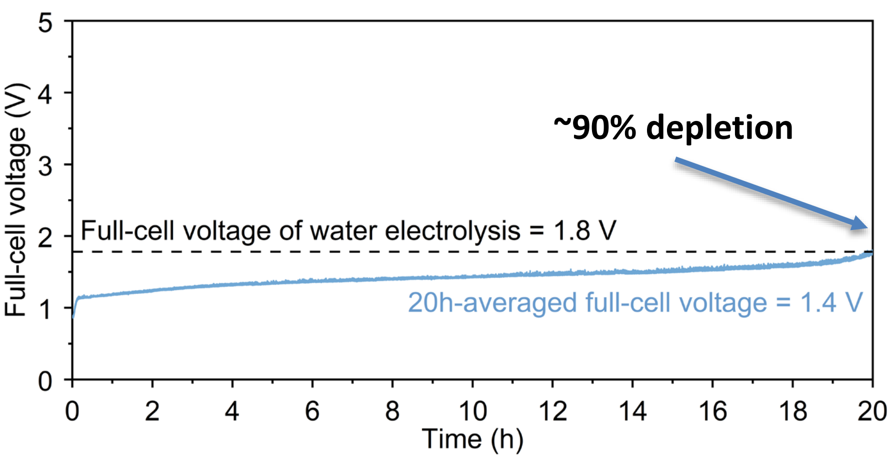
[a] We have reduced this a net revenue by subtracting the cost of compressing the CO_2
[b] https://doi.org/10.1002/ese3.956
[c] Appl. Sci. 2020, 10, 2946
[d] Wind electricity 11 gram/kWh
Note: using the same evaluation method, gray hydrogen has a carbon footprint of ~17 kg CO_2e/kg H_2.

Challenge #1: cell voltage increases after 10~12 hours

Galvanostatic test of crude glycerol over 21h



Galvanostatic test of glucose over 20h



- Glucose and crude glycerol may be oxidized to some harder-to-oxidize intermedia chemicals, such as tartaric acid, glyceric acid and glycolic acid.
- Depletion of biomass could be another factor.

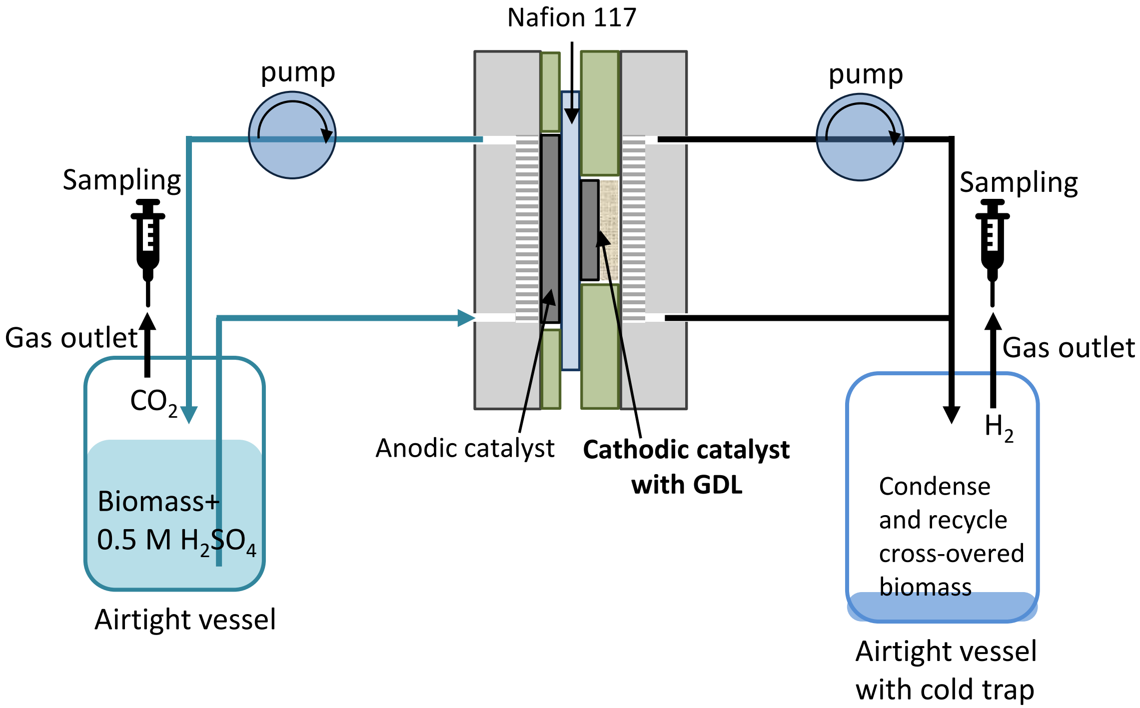
[1] Bioresource Technology 293 (2019) 122155

Challenge #2: Crude glycerol, glucose conversion and crossover

Biomass conversion & crossover analysis

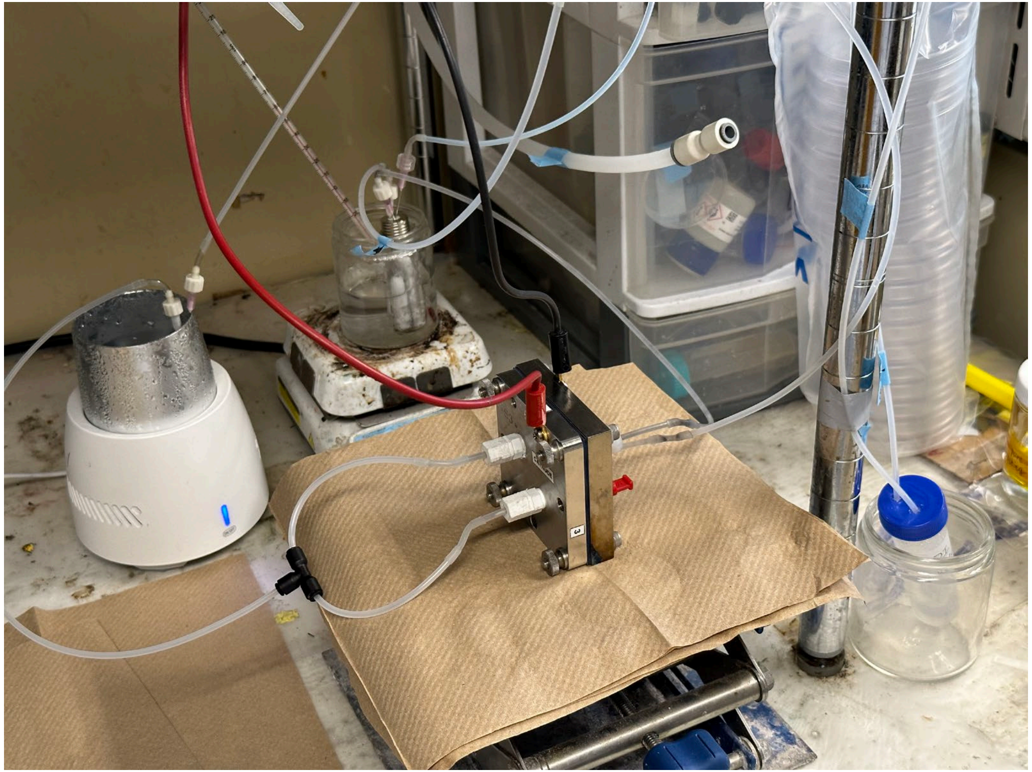
	Crude glycerol	Glucose
Conversion of non-cross-overed biomass at the anodic side	98%	89%
Crossover to catholyte	19%	2%
Overall biomass conversion	80%	87%

Proposed system optimization for solving crossover

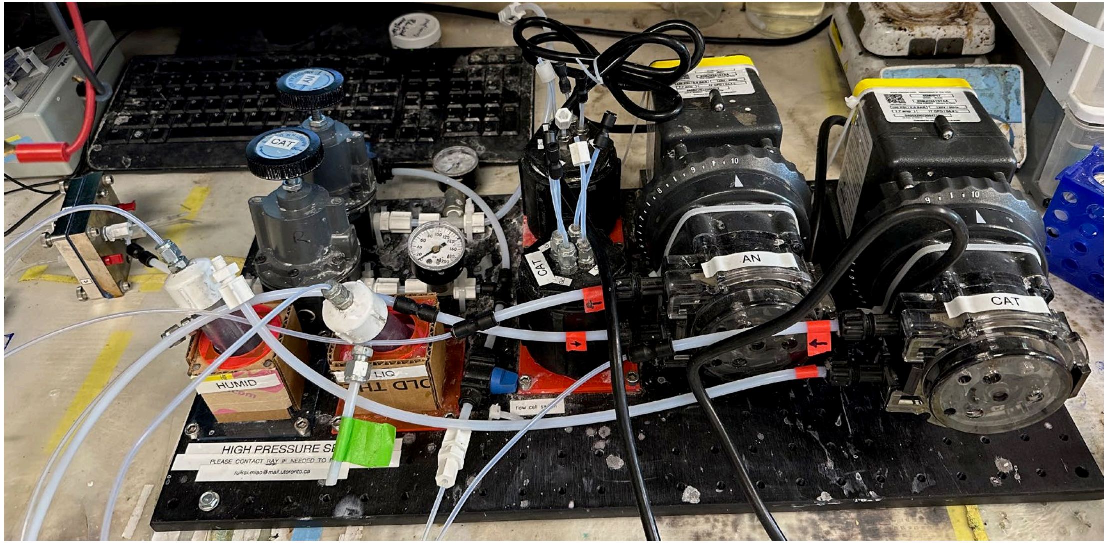


Challenge #2: Crude glycerol, glucose conversion and crossover

Photograph of system optimization to address crossover



10-bar setup



- All parts are resistance to 10 bar and H_2SO_4, and capable of holding and sampling high purity H_2 and CO_2
- To prevent pressure bias, we keep 10 bar at both the cathodic and anodic side by using back pressure regulators
- The system is purged by Ar to reach 10 bar before electrolysis

Path forward

Current stage and target

	Current stage	Target
Time averaged full-cell voltage (V)	1.1 (20h)	1
GJ / ton H_2	105	96
Biomass utilization (%)	87	98
Carbon crossover to catholyte (%)	2	1
Carbon footprint (ton CO_2/ton H_2)	-6.3	-7.8
Anodic CO_2 purity (%)	96	98
CO_2 and H_2 pressure (bar)	1	20

R&D topics

- Effect of salt in crude glycerol on electrochemical performance
- Membrane fouling over long-term electrolysis
- Effect of N and S impurities on the electrochemical performance
- Mechanism study on biomass electro-oxidation pathway
- Electrochemical performance, local environment, and reaction pathway change under 20 bar
- Innovative anodic catalyst discovery for biomass electro-oxidation