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Supplementary information

Development of an Aspen Plus® model for the process of hydrogen production by black liquor electrolysis

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Supplementary information

Mass balance

The mass balance provided the information needed to simulate the BL electrolysis (Table S1). The mass balance was obtained through BL electrolysis in a laboratory cell with the following conditions: T = 25 °C, N = 1, V_{cell} = 3.0 V, P = 1 bar, and W_{stack} = 0.915 W. The cell worked in batch operation for 3 hours.

Table S1. Mass balance based on BL electrolysis in a laboratory cell.

Component		Inlet (g)	Outlet (g)
Anode: Nickel plate		20.650	20.076
Cathode: Nickel plate		20.507	20.507
Black liquor	H_2O	264.720	264.454
	NaOH	3.574	3.574
	Na_2S	2.118	2.118
	Na_2SO_4	7.412	7.412
	KOH	10.920	10.920
	K_2CO_3	0.199	0.199
	K_2SO_4	0.596	0.596
	Lignin	4.798	4.598
	Sugars	2.214	2.214
	Hydroxy-carboxylic acids	0.417	0.417
	Acid Low MW volatiles	6.419	6.419
	Ni	0	0.026
	H_2	0	0.030
Solid	Ni	0	0.548
	O	0	0.172
	S	0	0.103
	Lignin	0	0.200
Total	344.543	344.543	344.581

The following assumptions were made to obtain the mass balance: (i) the formed gas was pure hydrogen, and (ii) hydrogen came only from the water. Due to the components simplifications described in section 2.3 of the paper, the mass balance used in Aspen Plus® is presented in Table S2.

Table S2. The mass balance used in Aspen Plus®.

Component	Inlet (mol/h)	Outlet (mol/h)
Ni (s)	0.1173	0.1140
H_2O	4.902	4.897
NaOH	0.02978	0.02978
Na^+	0.01810	0.01810
S^{2-}	9.050×10^{-3}	7.978×10^{-3}
Na_2SO_4	0.01669	0.01669
KOH	0.06488	0.06488
K_2CO_3	4.789×10^{-4}	4.789×10^{-4}
K_2SO_4	1.139×10^{-3}	1.139×10^{-3}
p-Coumaryl Alcohol	1.838×10^{-3}	1.762×10^{-3}
Glycose	4.095×10^{-3}	4.095×10^{-3}
Citric Acid	7.235×10^{-4}	7.235×10^{-3}
Acetic Acid	0.03560	0.03560
H_2	0	1.469×10^{-4}
Ni^{2+}	0	3.731×10^{-3}
O_2	0	1.865×10^{-3}
Anthracene	0	7.680×10^{-5}
S	0	1.073×10^{-3}
Total	5.202	5.204

From this mass balance, it is possible to extract useful information, such as the stoichiometric factors (Table S3).

Table S3. Stoichiometric factors for the different compounds.

Compounds	Stoichiometric factors
Acetic Acid	0
Citric Acid	0
p-Coumaryl Alcohol	−0.0155
Anthracene	0.0155
Glycose	0
H_2	1
H_2O	−0.993
K_2CO_3	0
K_2SO_4	0
KOH	0
Na_2SO_4	0
Na^+	0
NaOH	0
Ni	−0.656
Ni^{2+}	0.751
O_2	0.376
S	0.216
S^{2-}	−0.216

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Batch operation vs. continuous operation

Figures S1 and S2 compare the experimental data and the adjusted polarization curve, both for batch and continuous operation.

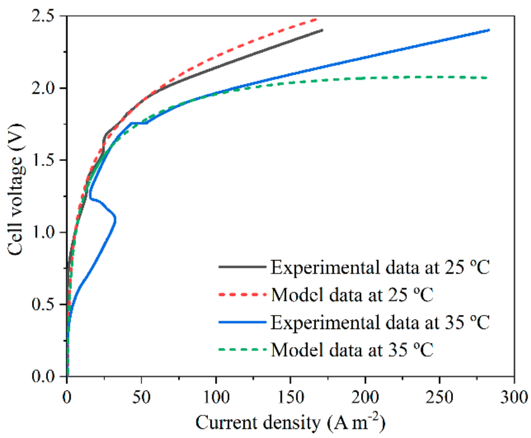
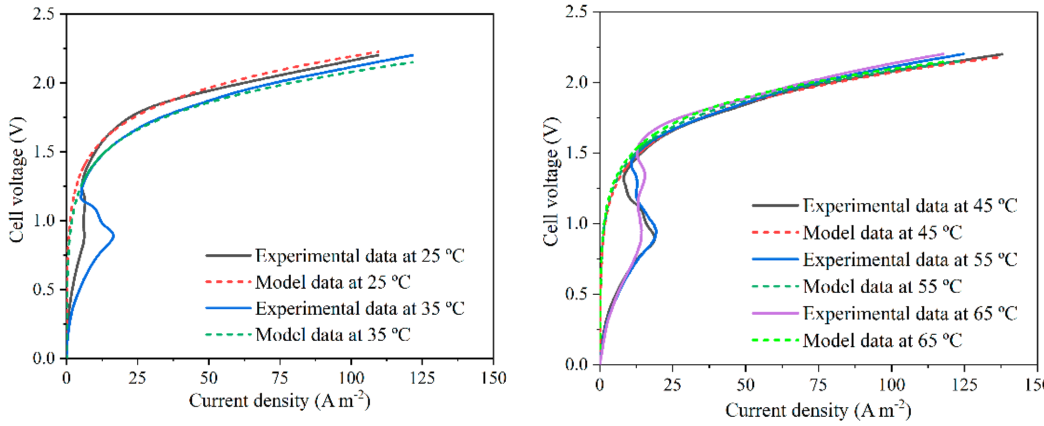


Figure S1. Comparison between experimental data and the model for batch simulation at 25 °C and 35 °C.



a) **b)**

Figure S2. Comparison between experimental data and the model at different temperatures for continuous operation.

Sensitivity analysis

This section shows the electrolyzer sensitivity analysis data to understand how each variable influences the others.

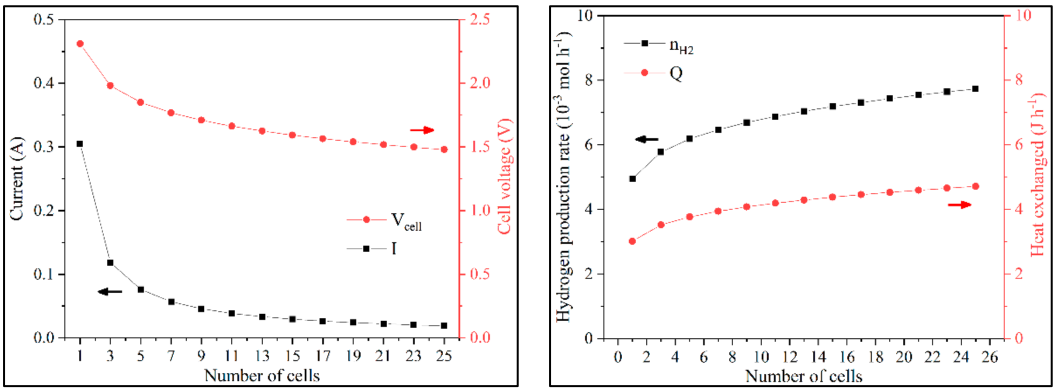


Figure S3. Variation of i, V_{cell}, n_{H2}, and Q_T with N in continuous operation.

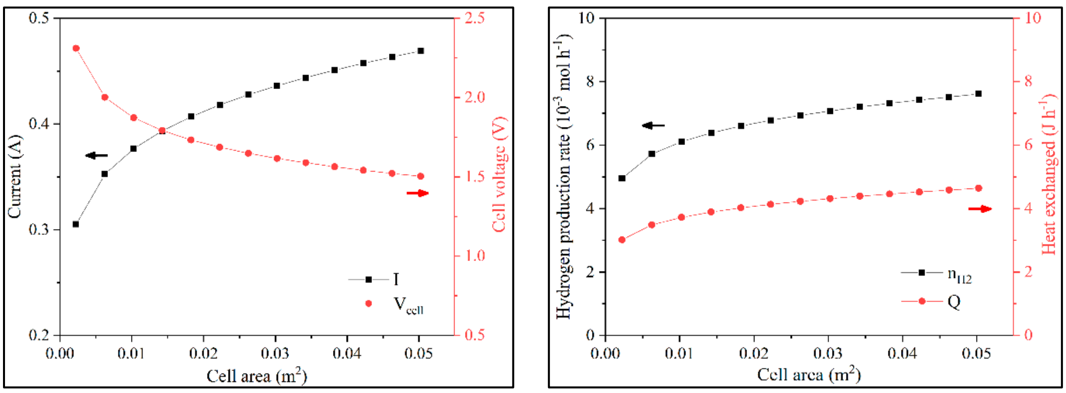


Figure S4. Variation of i, V_{cell}, n_{H2}, and Q_T with A_{cell} in continuous operation.

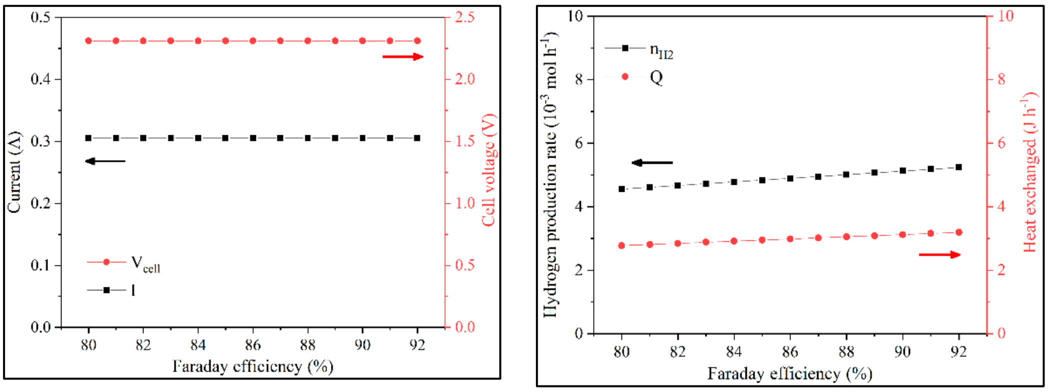


Figure S5. Variation of i, V_{cell}, n_{H2}, and Q_T with the Faraday efficiency in continuous operation.

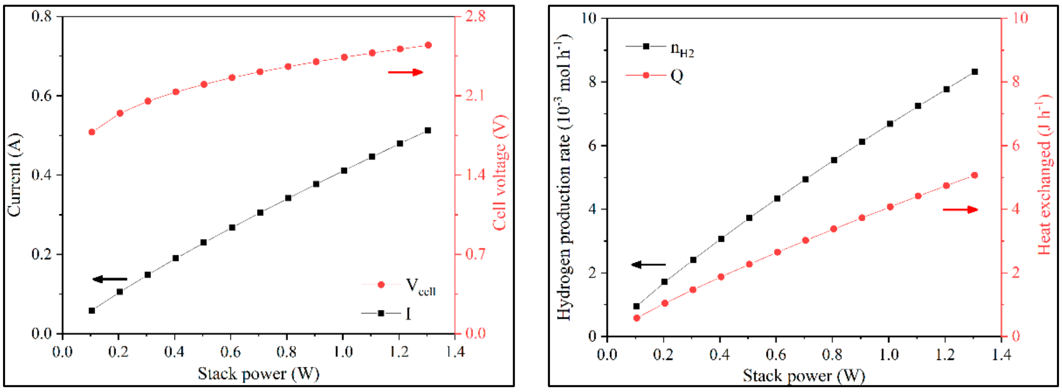


Figure S6. Variation of i, V_{cell}, n_{H2}, and Q_T with the electric power in continuous operation.

Table S4. Sensitivity analysis for Faraday efficiency.

Efficiency Increment (%)	Batch operation				Continuous operation			
	Δi (%)	ΔV_{cell} (%)	Δn_{H2} (%)	ΔQ_T (%)	Δi (%)	ΔV_{cell} (%)	Δn_{H2} (%)	ΔQ_T (%)
−5.75	0	0	−5.75	−5.75	0	0	−5.75	−5.75
−3.45	0	0	−3.45	−3.45	0	0	−3.45	−3.45
3.45	0	0	3.45	3.45	0	0	3.45	3.45
5.75	0	0	5.75	5.75	0	0	5.75	5.75

Table S5. Sensitivity analysis for temperature.

T Increment (%)	Batch operation				Continuous operation			
	Δi (%)	ΔV_{cell} (%)	Δn_{H2} (%)	ΔQ_T (%)	Δi (%)	ΔV_{cell} (%)	Δn_{H2} (%)	ΔQ_T (%)
16	1.28	−1.26	1.28	4.27	2.54	−2.48	2.54	14.54
28	3.99	−3.84	3.99	12.99	3.78	−3.64	3.78	24.82
32	6.96	−6.51	6.96	19.00	4.55	−4.35	4.55	34.66
40	15.98	−13.78	15.98	34.11	5.08	−4.84	5.08	81.09