

Electronic Supplementary Information (ESI)

Can Sustainable Ammonia Synthesis Pathways Compete with Fossil-Fuel Based Haber-Bosch Processes?

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Supplementary Figures

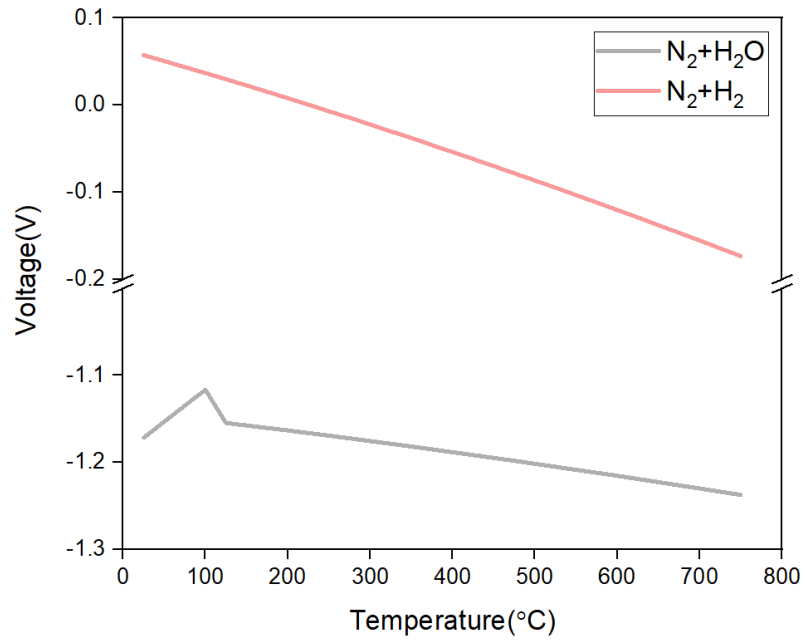


Figure S1. Reaction voltages at different temperatures. Related to Table 1.

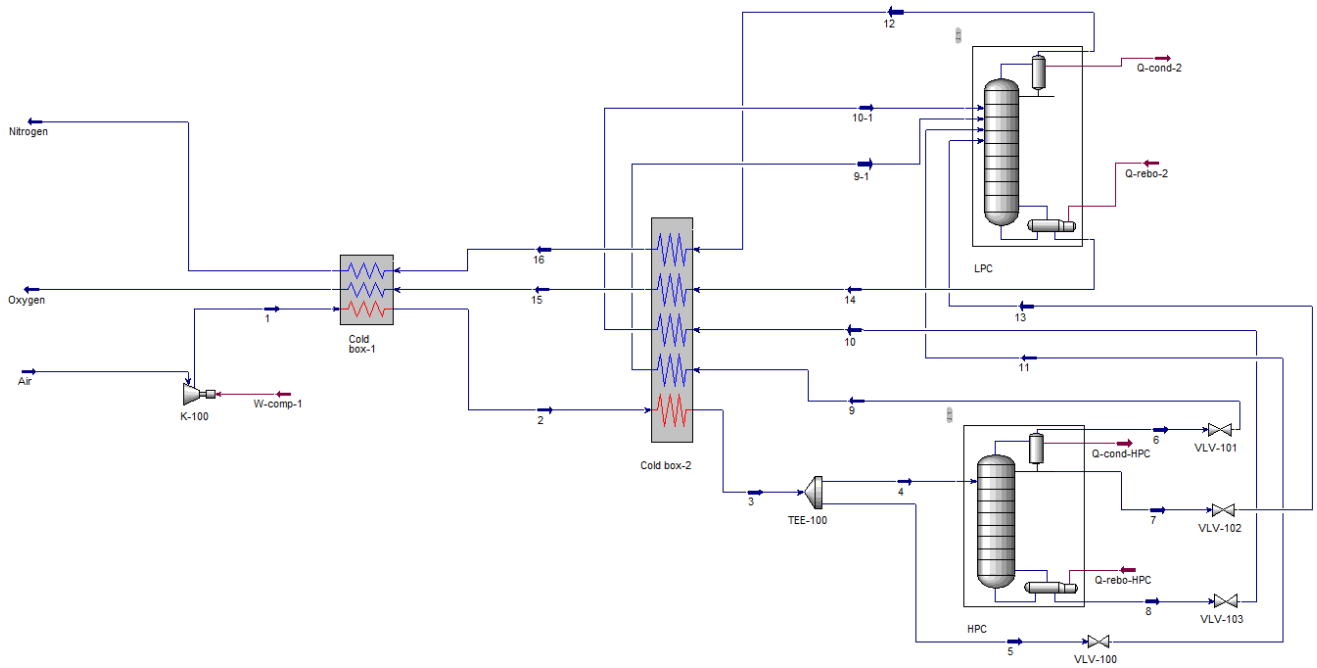


Figure S2. Process flow diagram for air separation to produce N₂. The air separation unit is used in Stage 2. Related to Figures 2-5.

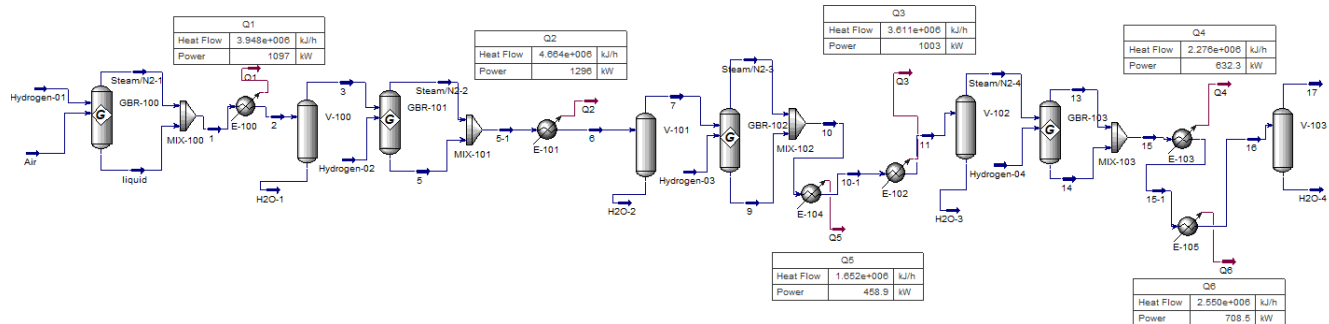


Figure S3. Process flow diagram for oxygen removal unit as used in Stage 3 pathways. Related to Figures 2-5.

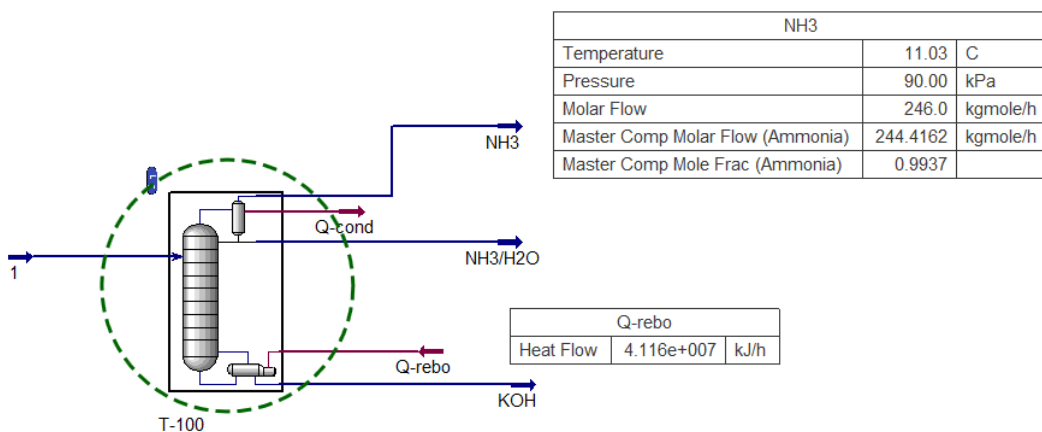


Figure S4. Distillation process flow diagram for NH₃ separation from electrolyte in room temperature (RT) electrosynthesis. Related to Figures 2-5.

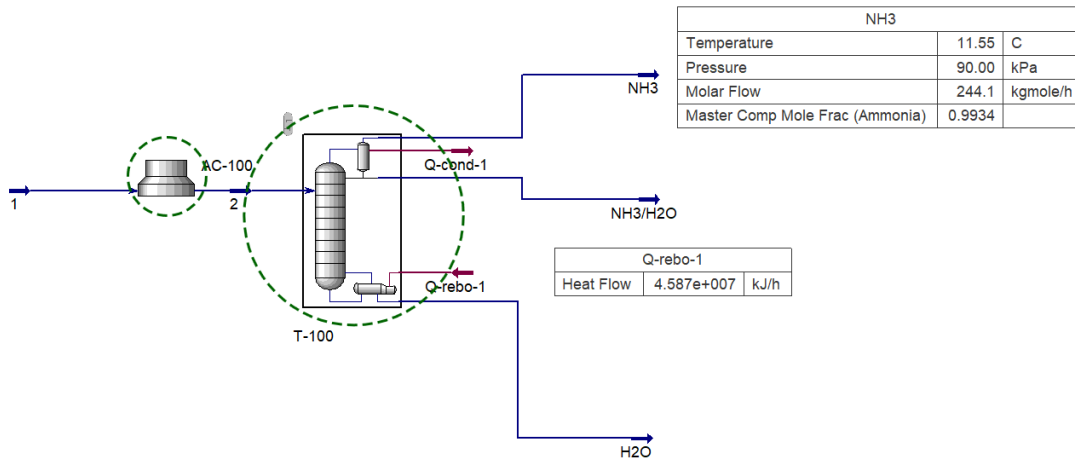


Figure S5. Distillation process flow diagram for three-step e-NH₃ in Stage 3 pathway. Related to Figures 2-5.

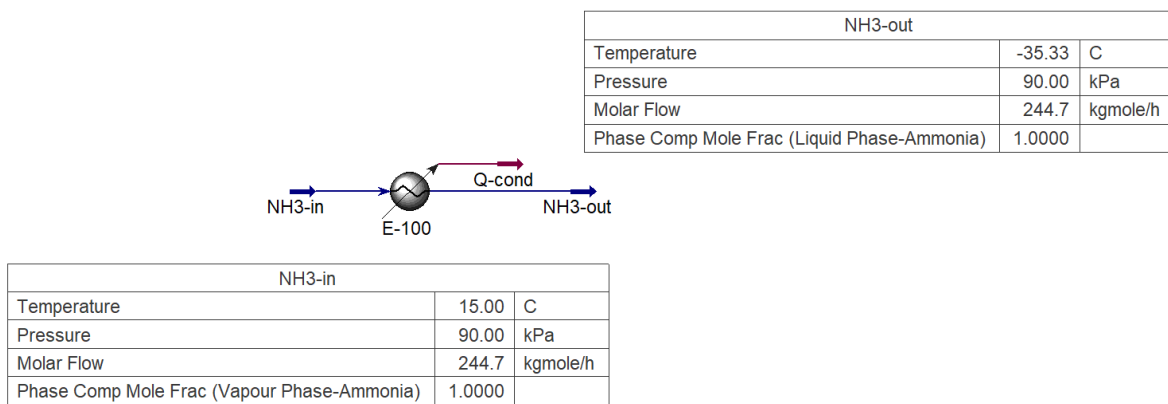
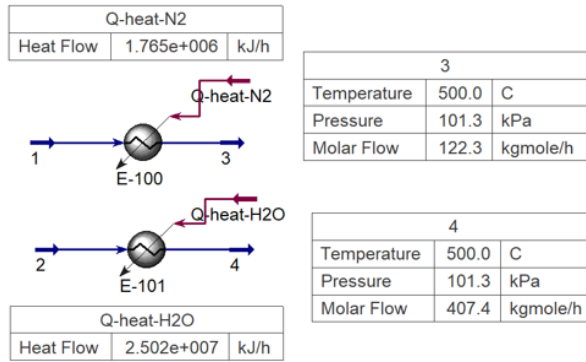


Figure S6. Condensation process of NH₃ as required in Stage 2. Related to Figures 2-5.

a) Simulation for N₂ and H₂O heating



b) Simulation for N₂ and H₂ heating

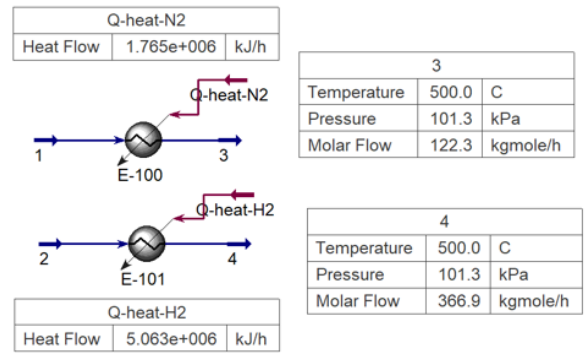


Figure S7. One-step and two-step e-NH₃ in Stage 3 were evaluated both at room temperature (RT) at 25 °C and high temperature (HT) at 500 °C. Aspen model is shown here for HT case wherein heating up the feed was required. a) N₂ and H₂O heating in one-step e-NH₃ and b) N₂ and H₂ heating in two-step e-NH₃. Related to Figures 2-5.

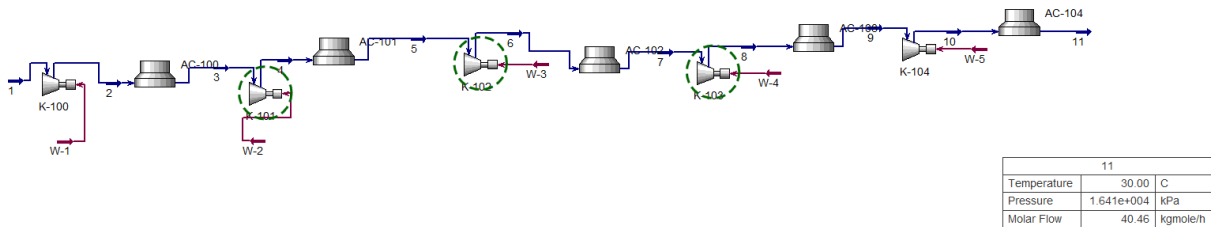


Figure S8. Aspen simulation for O₂ compression. The O₂ is produced from anodic reaction in water electrolysis, NH₃ electrosynthesis and LiOH electrolysis reactions.

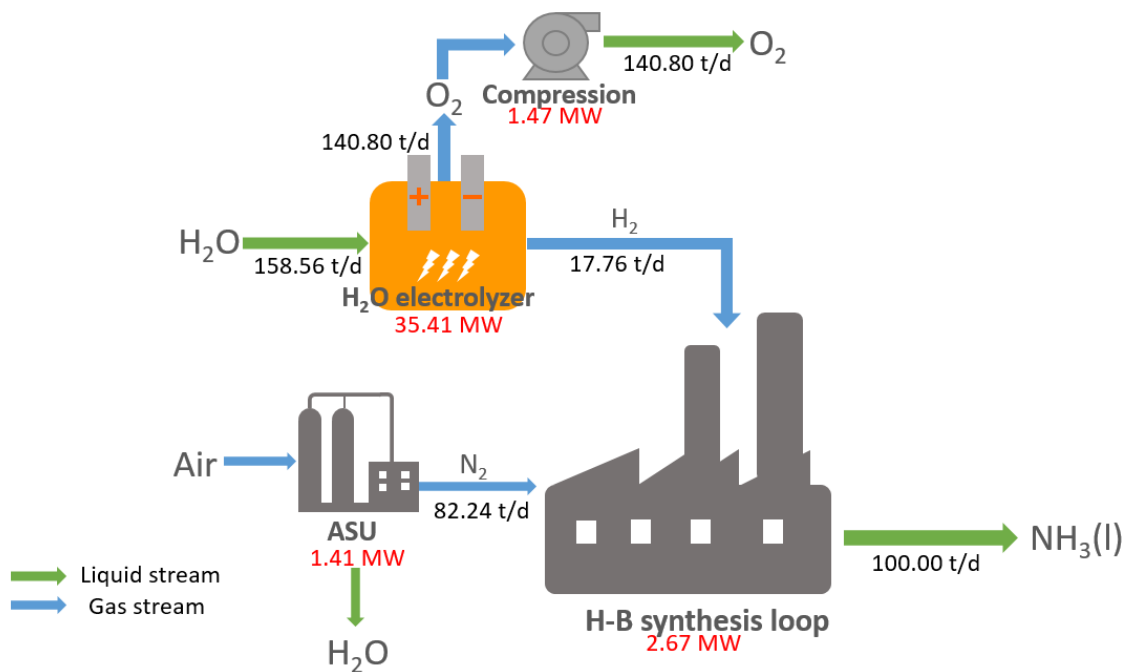


Figure S9. Process flow diagram for Stage 2. The HB synthesis loop here includes compressors, heat exchangers, reactors, and other supplementary equipment. Related to Figures 2-5.

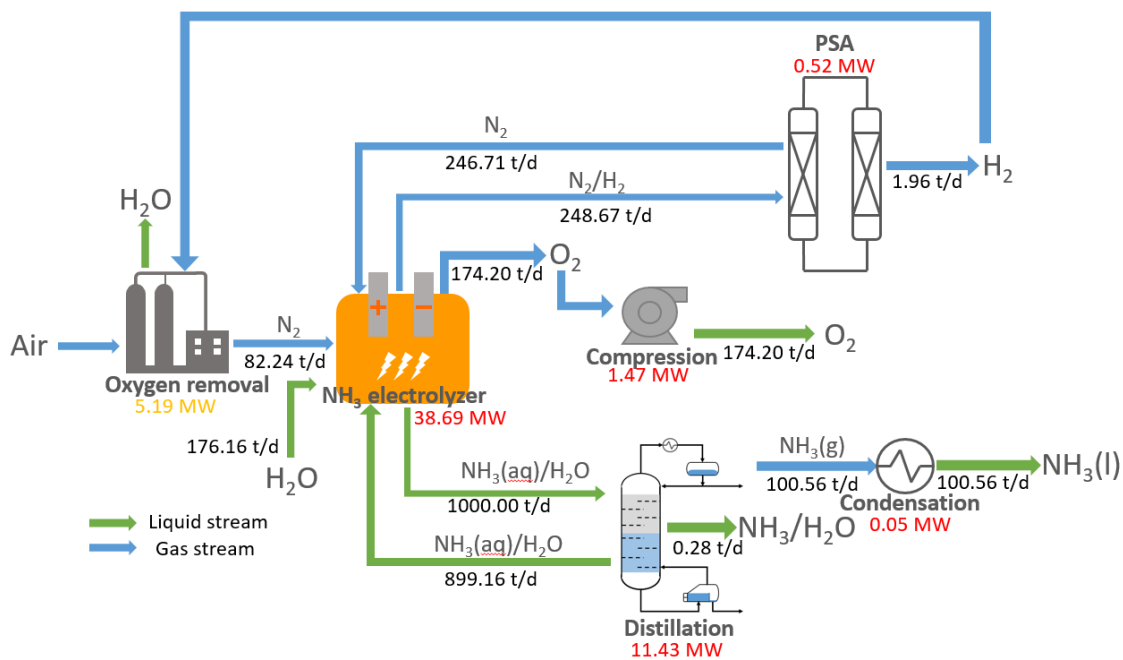


Figure S10. Process flow diagram for Stage 3 one-step e-NH₃ at room temperature. Related to Figures 2-5.

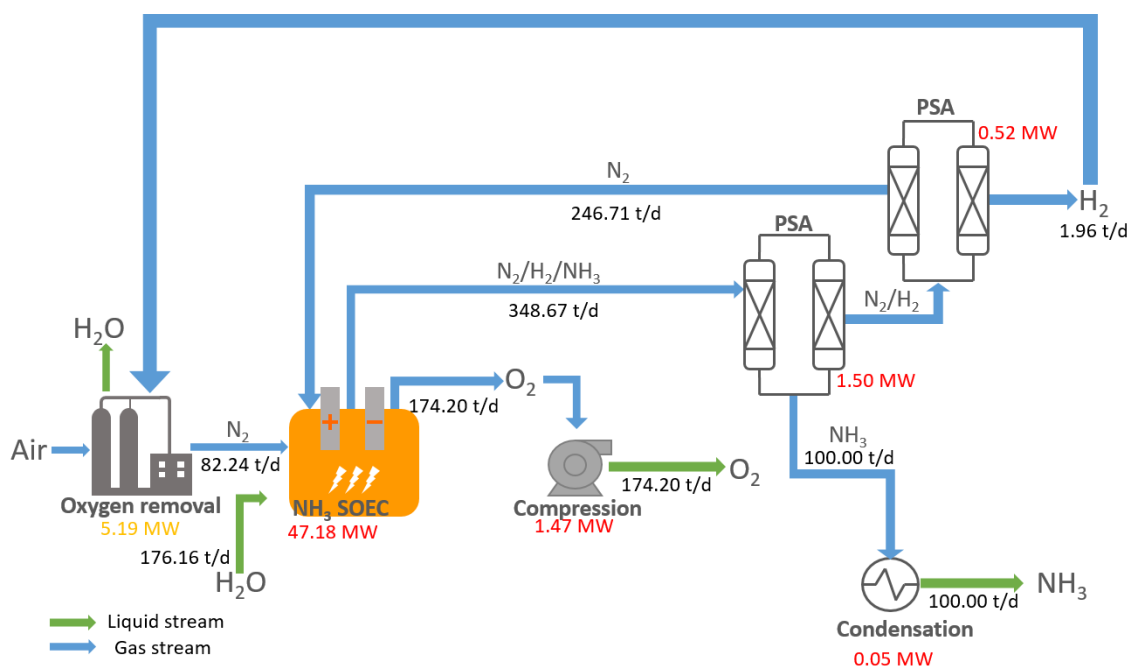


Figure S11. Process flow diagram for Stage 3 one-step e-NH₃ at high temperature (500 °C). Related to Figures 2-5.

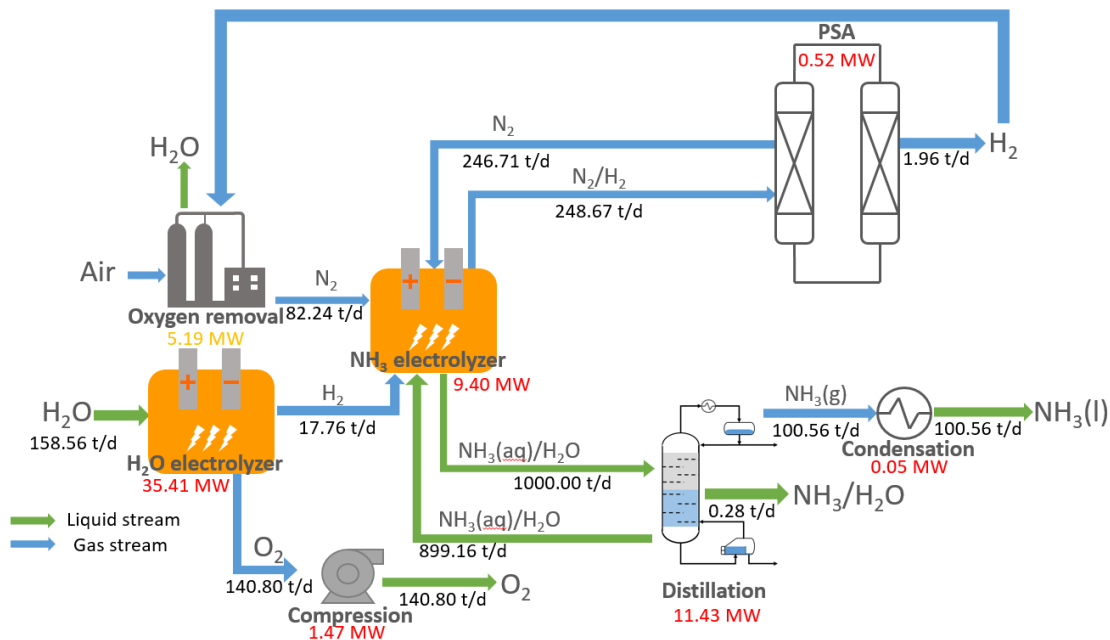


Figure S12. Process flow diagram for Stage 3 two-step e-NH₃ at room temperature. Related to Figures 2-5.

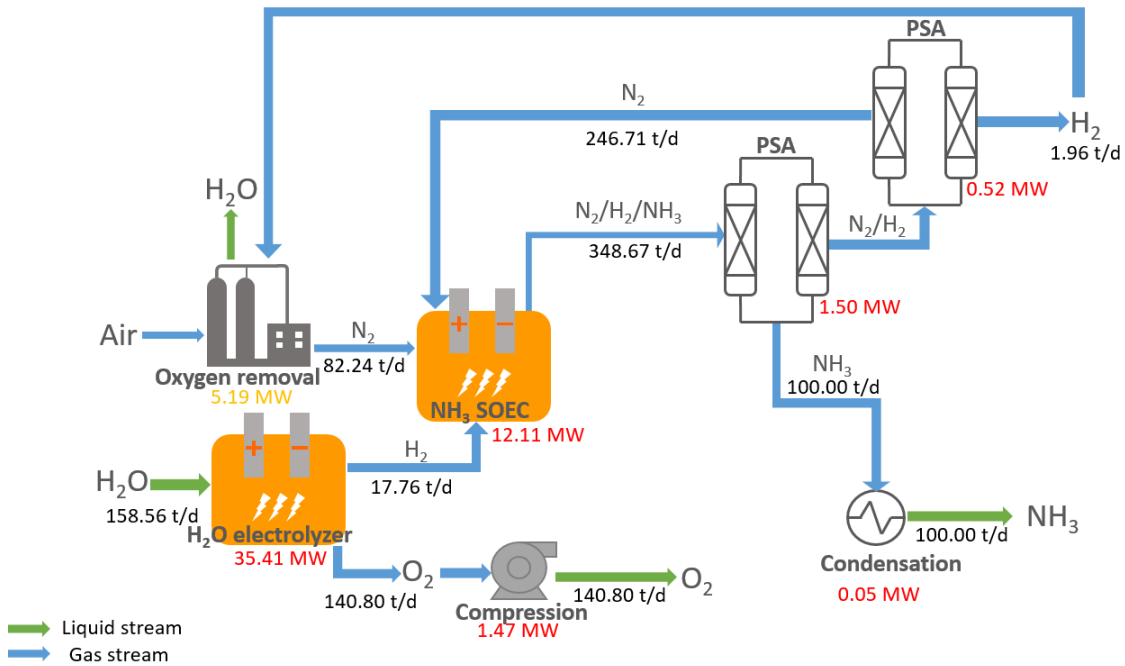


Figure S13. Process flow diagram for Stage 3 two-step e-NH₃ at high temperature (500 °C). Related to Figures 2-5.

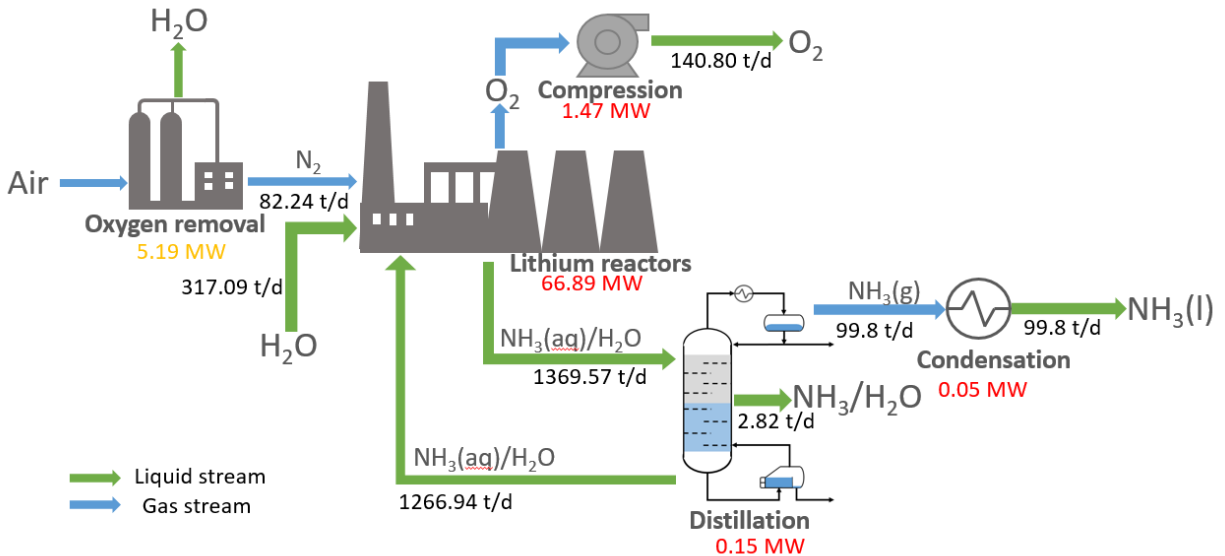
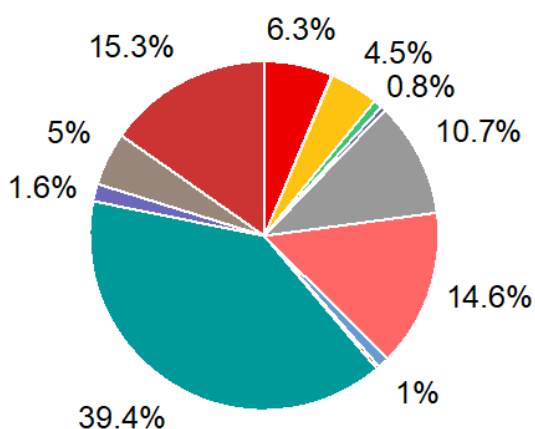
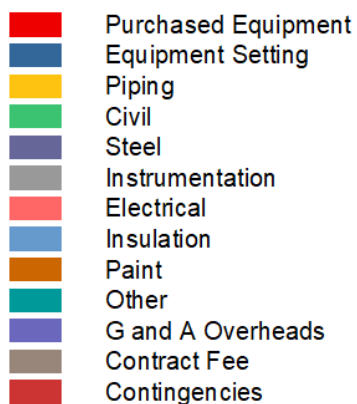


Figure S14. Process flow diagram for Stage 3 three-step e-NH₃. Here, lithium reactors contain the electrolyzers for LiOH electrolysis, the reactors for Li₃N production and NH₃ synthesis. Related to Figures 2-5.

a) Capital cost breakdown



b) Operating cost breakdown

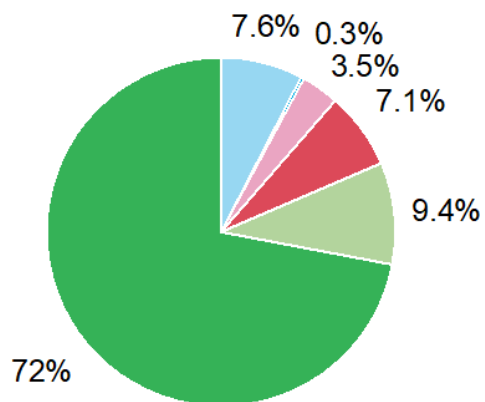
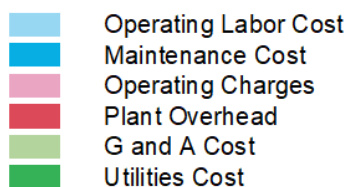


Figure S15. Cost breakdown for the distillation process in Stage 3 one-step e-NH₃ at room temperature: a) capital cost breakdown to demonstrate various direct and indirect costs considered, and b) operating cost to illustrate various fixed and variable costs considered in this study. Related to Figure 3.

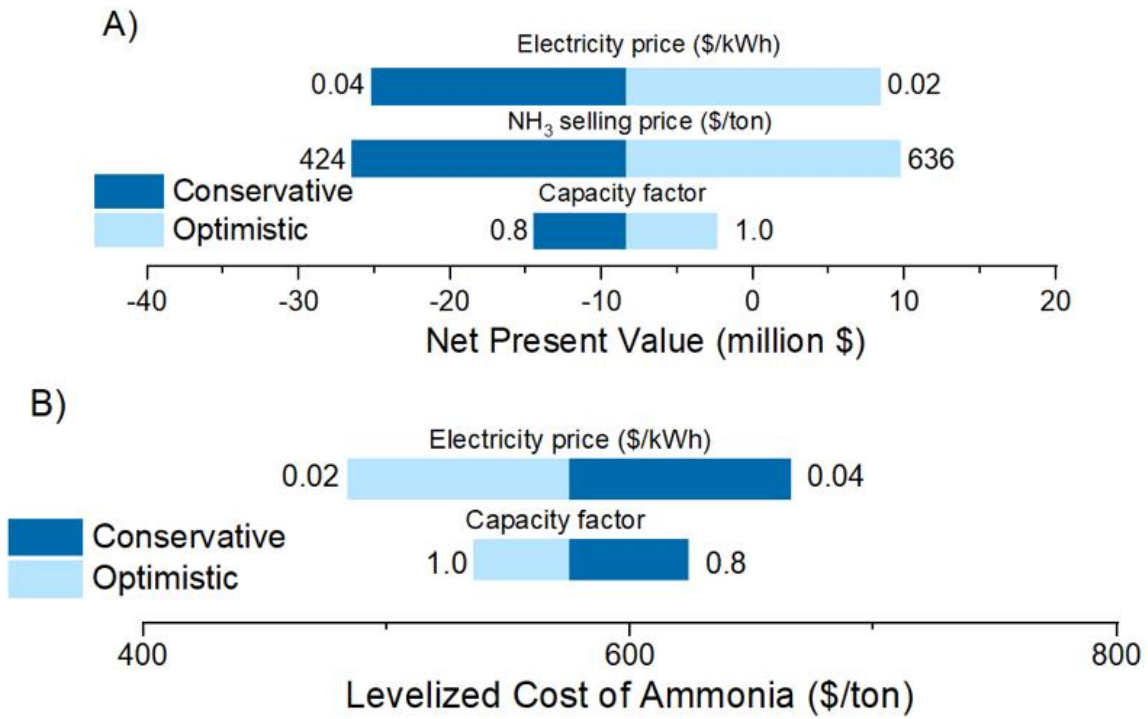


Figure S16. Sensitivity analysis on a) NPV and b) LCOA for Stage 2. The range of values for sensitivity analysis is shown in Table S14. Related to Figure 4.

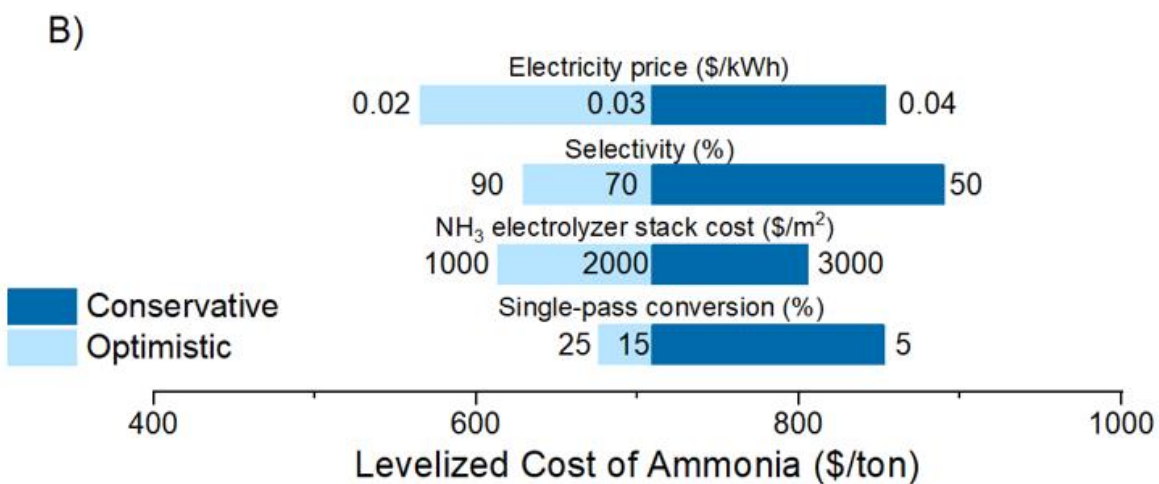
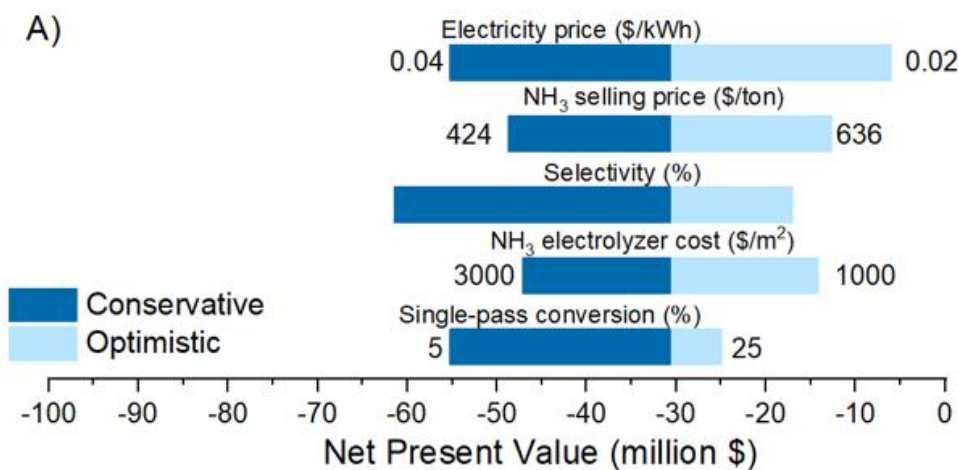


Figure S17. Sensitivity analysis on a) NPV and b) LCOA for Stage 3 one-step e-NH₃ at room temperature. The range of values for sensitivity analysis is shown in Table S14. Related to Figure 4.

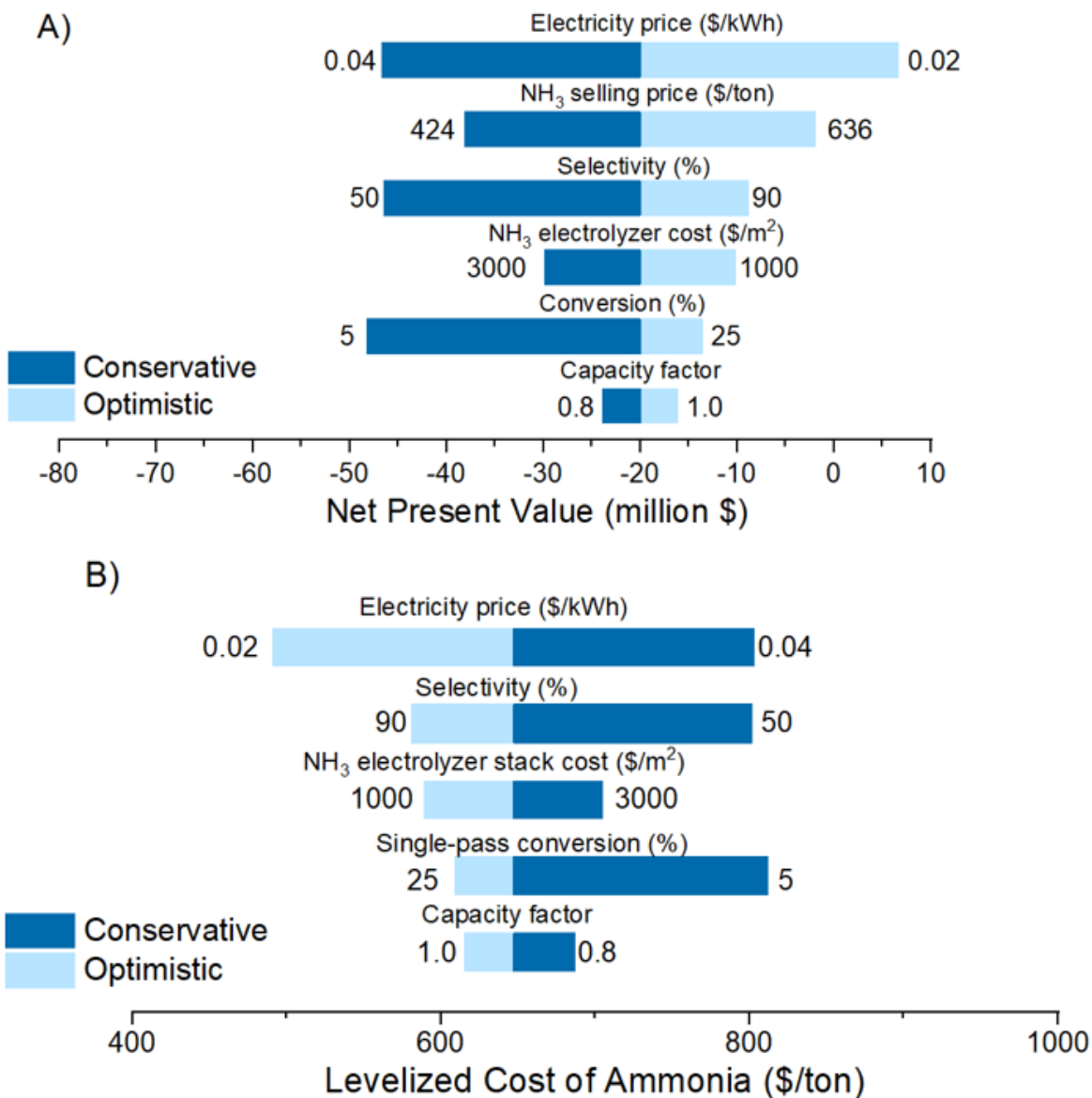


Figure S18. Sensitivity analysis on a) NPV and b) LCOA for Stage 3 one-step e-NH₃ at high temperature. The range of values for sensitivity analysis is shown in Table S14. Related to Figure 4.

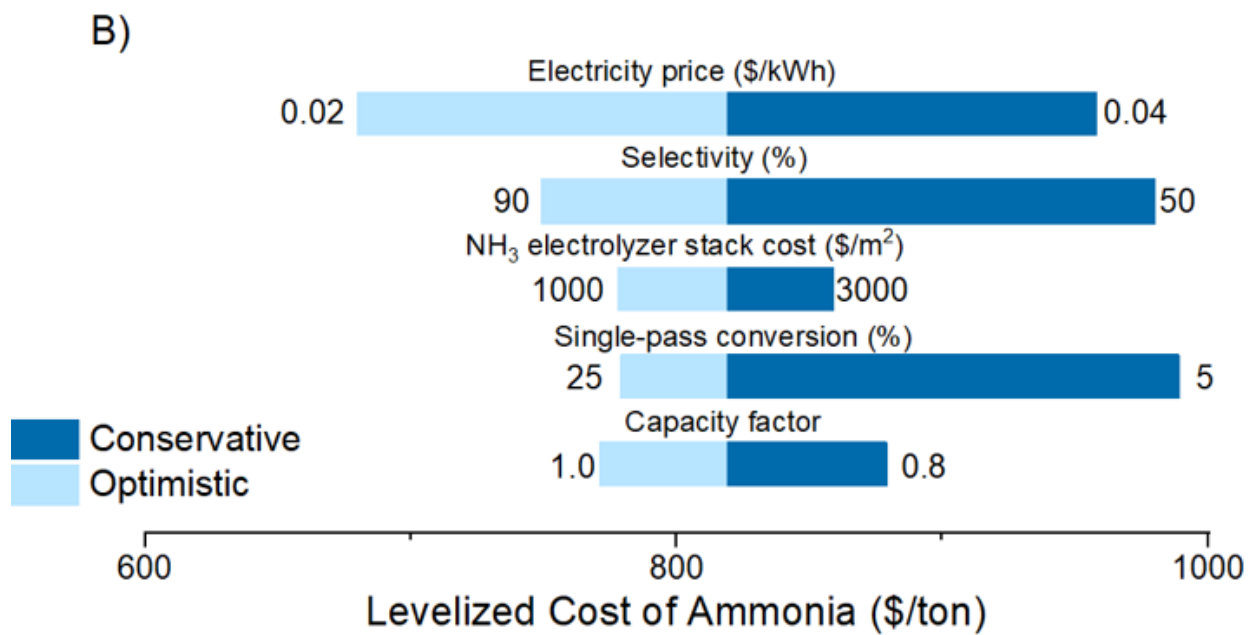
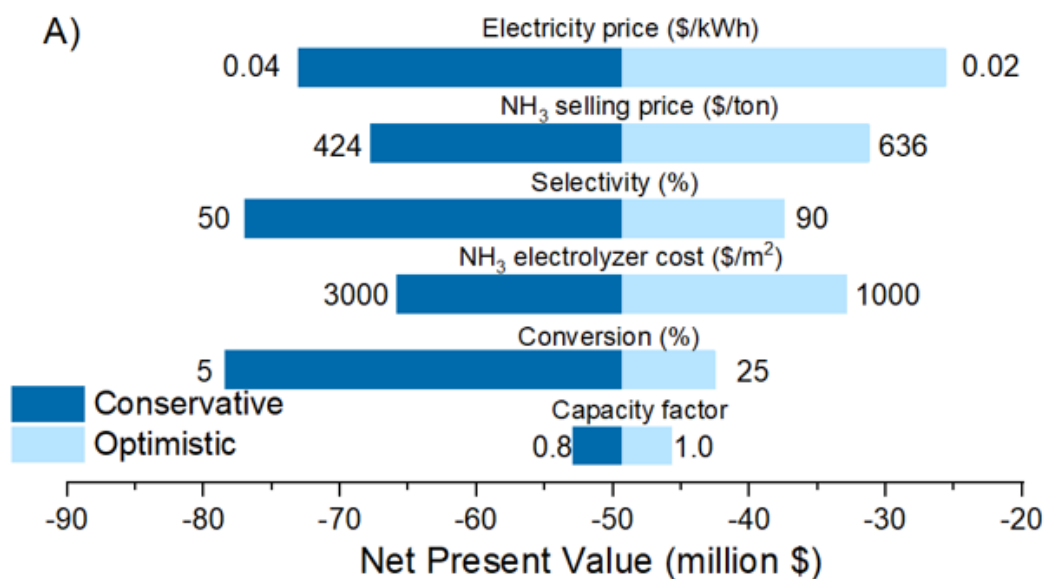


Figure S19. Sensitivity analysis on a) NPV and b) LCOA for Stage 3 two-step e-NH₃ at room temperature. The range of values for sensitivity analysis is shown in Table S14. Related to Figure 4.

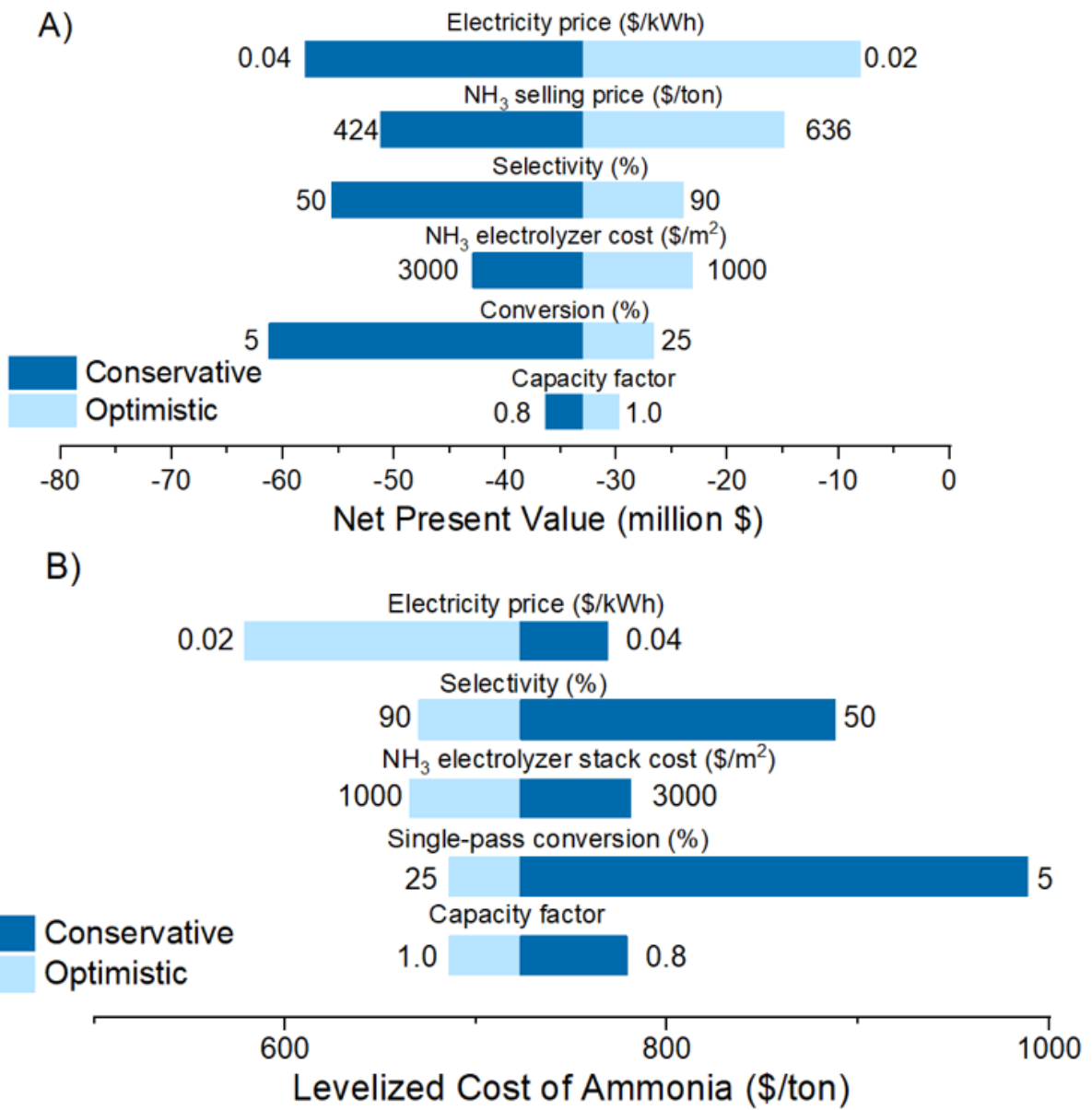


Figure S20. Sensitivity analysis on a) NPV and b) LCOA for Stage 3 two-step e-NH₃ at high temperature. The range of values for sensitivity analysis is shown in Table S14. Related to Figure 4.

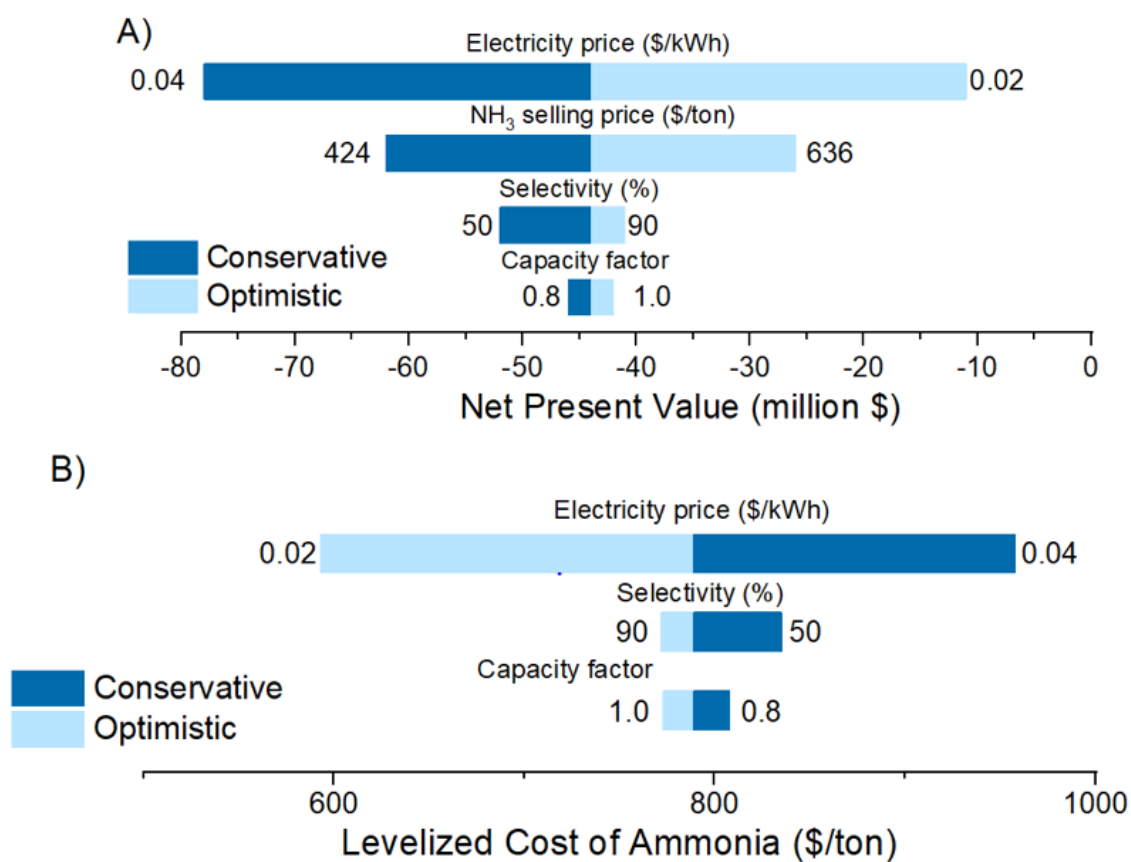


Figure S21. Sensitivity analysis on a) NPV and b) LCOA for Stage 3 three-step e-NH₃. The range of values for sensitivity analysis is shown in Table S14. Related to Figure 4.

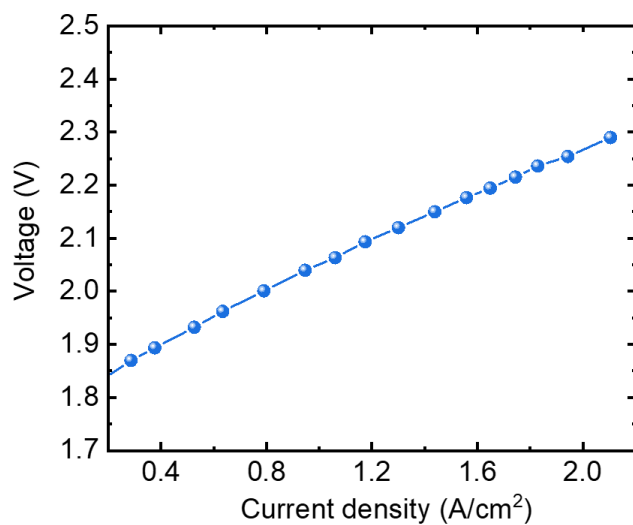


Figure S22. Current density-Voltage relationship as adopted from Siemens water electrolyzer.⁴¹ This i-V behavior was assumed as a representative model to reveal their impact on the economic feasibility of one-step NH_3 electrolysis, as shown in Fig 4B in the manuscript.

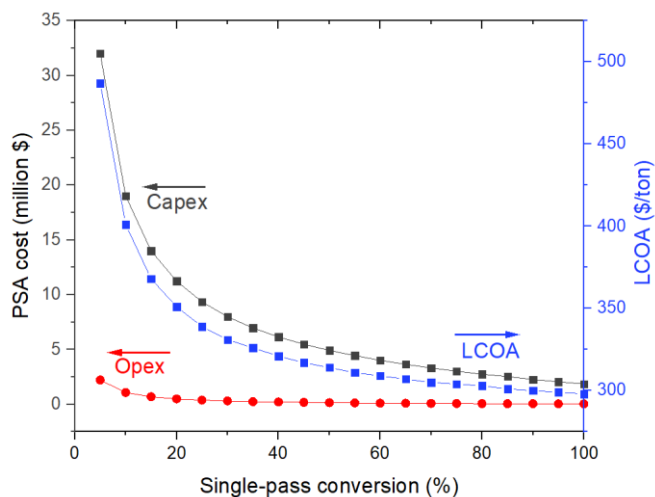


Figure S23. The impact of single-pass conversion efficiency of the capex and opex of pressure swing absorption (PSA) for NH_3 separation in Stage 3 one-step e-NH_3 .

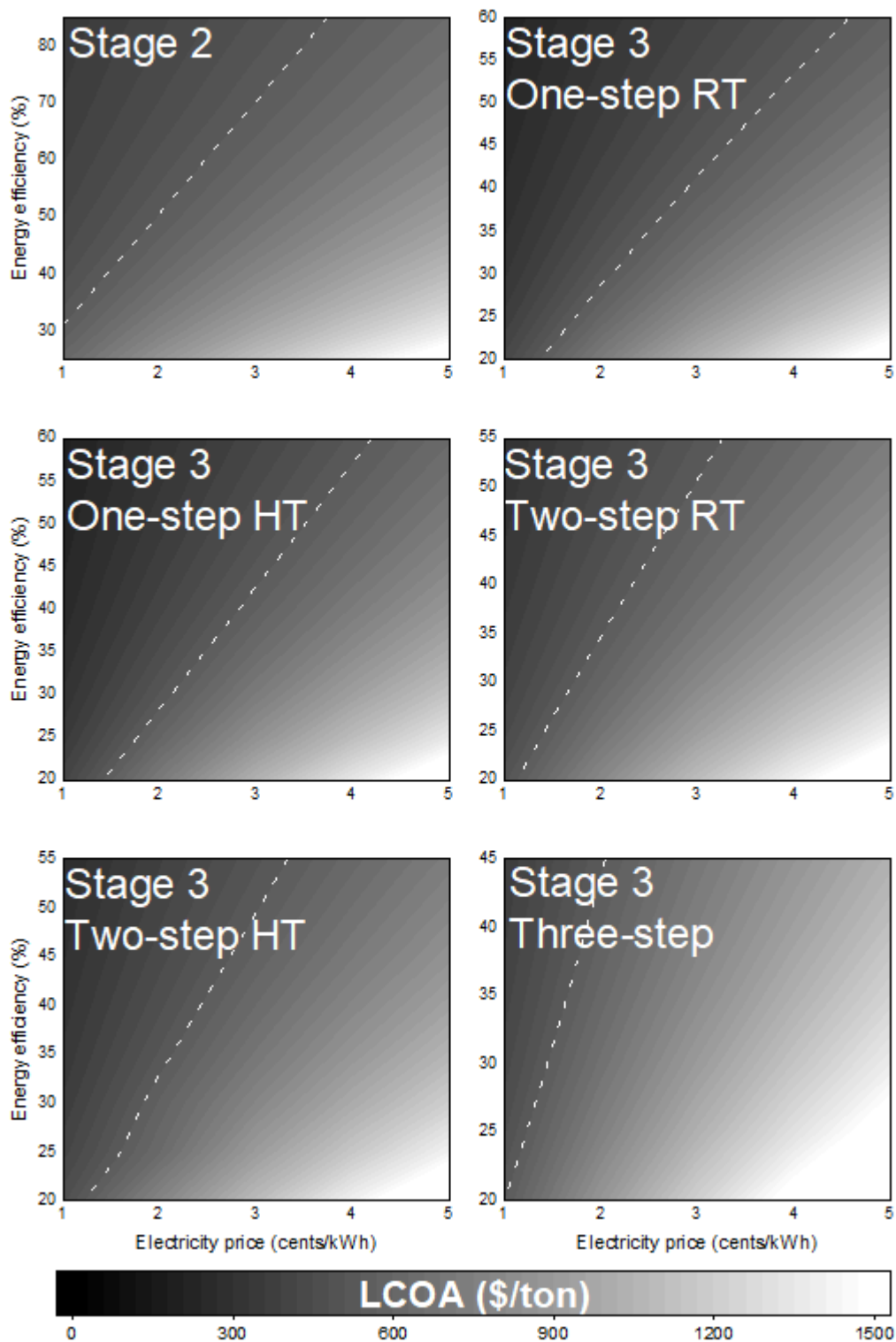


Figure S24. Levelized cost of NH₃ electro-synthesis pathways. The contour plots show overall energy efficiency versus electricity price. All graphs are constructed under long-term prediction (Table S9). The dashed white lines on the plots represent NH₃ market price from incumbent SMR-HB process at large scale (\$530/ton).

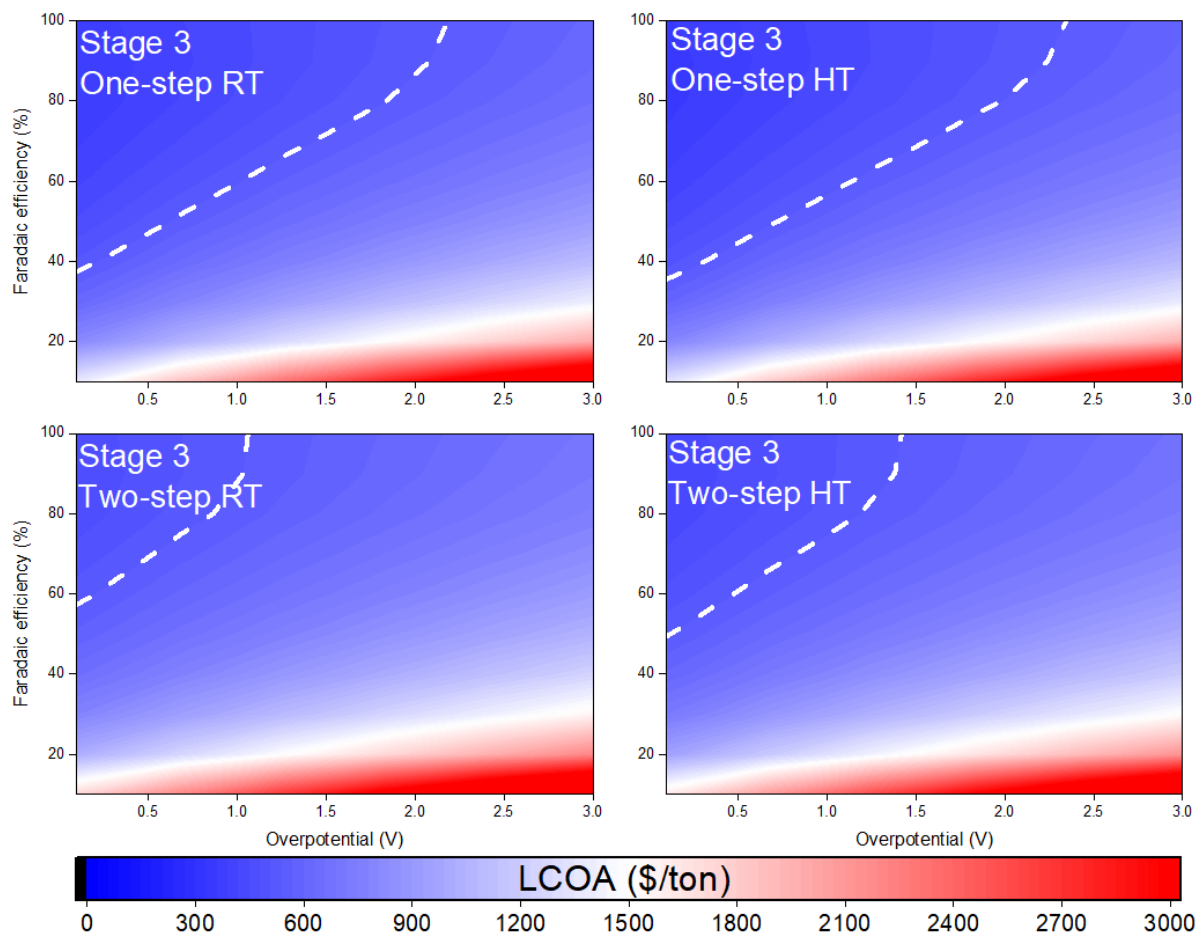


Figure S25. Levelized cost of NH₃ electro-synthesis pathways. The contour plots show faradaic efficiency versus overpotential. All graphs are constructed under long-term process assumptions (Table S9). The dashed white lines on the plots represent NH₃ market price from incumbent SMR-HB process at large scale (\$530/ton).

Supplementary Tables

Table S1. Heat capacity data.¹ Related to Table 1.

	A	B*10 ³	C*10 ⁶	D*10 ⁻⁵	E*10 ⁹
N ₂	3.28	0.59		0.04	
H ₂	3.25	0.42		0.08	
O ₂	3.64	0.51		-0.23	
H ₂ O(g)	3.47	1.45		0.121	
H ₂ O(l)	9.07				
NH ₃	3.58	3.02		-0.19	

Table S2. Entropy data.¹ Related to Table 1.

	ΔS (J/Mole K)
N ₂	191.61
H ₂	130.68
O ₂	205.15
H ₂ O(g)	188.84
H ₂ O(l)	69.95
NH ₃	192.77

Table S3. Enthalpies, Gibbs free energies and reaction voltages at various temperature. Related to Table 1.

	ΔH (J/4 mole NH ₃)	ΔG (J/4 mole NH ₃)	E_{rxn} (V)
Room-temperature one-step e-NH ₃	1530511.93	1356506.22	-1.17
High-temperature one-step e-NH ₃	1290818.07	1391112.64	-1.20
Room-temperature two-step e-NH ₃	-92219.72	-103584.38	0.06
High-temperature two-step e-NH ₃	-103077.67	50090.30	-0.09

Table S4. Cost comparison using different electrolytes for Stage 3 one-step e-NH₃. Related to Figures 2-5.

Separation process	Capital cost (\$)	Operating cost (\$/year)
Distillation (NH ₃ /KOH)	2,894,110	2,068,316
Distillation and PSA (NH ₃ /HCl)	2,972,854	3,608,340

Table S5. Detailed stream data for distillation (for Stage 3, one-step and two-step e-NH₃ at room temperature (RT)). Related to Figures 2-5.

	Unit	1	NH ₃	KOH	NH ₃ /H ₂ O
Vapour Fraction		0.00	1.00	0.00	0.00
Temperature	°C	25.00	11.03	102.83	11.03
Pressure	kPa	100.00	90.00	110.00	90.00
Molar Flow	kgmole/h	2251.34	245.95	2004.71	0.67
Mass Flow	kg/h	41667.00	4190.26	37464.83	11.91
Liquid Volume Flow	m ³ /h	49.75	13.12	36.62	0.02
Heat Flow	kJ/h	-599178104.19	-11723328.22	-567283084.64	-142199.06
Comp Mole Frac (Potassium-Hydroxide)		0.02	0.00	0.02	0.00
Comp Mole Frac (Ammonia)		0.11	0.99	0.00	0.36
Comp Mole Frac (Water)		0.88	0.01	0.98	0.64

Table S6. Detailed stream data for distillation column (for Stage 3, three-step e-NH₃). Related to Figures 2-5.

	Unit	1	2	NH ₃	NH ₃ /H ₂ O	H ₂ O
Vapour Fraction		1.00	0.00	1.00	0.00	0.00
Temperature	°C	450.00	30.00	11.55	11.55	102.31
Pressure	kPa	100.00	100.00	90.00	90.00	110.00
Molar Flow	kgmole/h	3181.00	3181.00	244.09	6.66	2930.25
Mass Flow	kg/h	57065.41	57065.41	4158.58	117.55	52789.28
Liquid Volume Flow	m ³ /h	66.11	66.11	13.02	0.20	52.89
Heat Flow	kJ/h	672659929.41	-857655505.36	-11644896.55	-1407028.78	-820456848.53
Comp Mole Frac (Ammonia)		0.08	0.08	0.99	0.36	0.00
Comp Mole Frac (Water)		0.92	0.92	0.01	0.64	1.00

Table S7. Detailed stream data for condensation. Related to Figures 2-5.

	Unit	NH ₃ (Distillation)-in	NH ₃ (Distillation)-out	NH ₃ (PSA)-in	NH ₃ (PSA)-out
Vapour Fraction		1	0	1	0
Temperature	°C	15.00	-35.33	10.00	-35.00
Pressure	<i>kPa</i>	90.00	90.00	100.00	100.00
Molar Flow	<i>kgmole/h</i>	244.67	244.67	244.67	244.67
Mass Flow	<i>kg/h</i>	4166.73	4166.73	4166.73	4166.73
Liquid Volume Flow	<i>m³/h</i>	6.76	6.76	6.76	6.76
Heat Flow	<i>kJ/h</i>	-11284084.73	-17542567.33	-11329261.50	-17536489.07
Comp Mole Frac (Ammonia)		1.00	1.00	1.00	1.00

Table S8. Basis for economic analysis. Related to Figures 2-5, and Table 2.

Parameters		Value
Ammonia production rate	ton/day	100
Plant life	Years	20
Working days	Day/year	350
Income tax	%	38.9
Nominal interest rate (NIR)	%	10
Salvage value	%	20
Location	North America	

Table S9. Process model assumptions. Related to Figures 2-5, and Table 2.

Process	Parameters	Units	Short-term prediction	Long-term prediction
	Electricity price	\$/kWh	0.03	0.02
	Ammonia price	\$/ton	530	636
NH ₃ electrosynthesis (e-NH ₃)	Current density	A/cm ²	0.3 (RT) 0.5 (HT)	0.5 (RT) 0.7 (HT)
	Cathode overpotential	V	0.5	0.3
	Anode overpotential	V	0.07 (H ₂) 0.3 (H ₂ O)	0.07 (H ₂) 0.3 (H ₂ O)
	NH ₃ selectivity	%	70	90
	N ₂ single-pass conversion	%	15	25
	NH ₃ electrolyzer stack cost	\$/m ²	2000	1000
	PEM H ₂ O electrolyzer stack cost	\$/m ²	13000	7700
H ₂ O electrolysis (e-H ₂ O)	Current density	A/cm ²	2.0	3.0
	Cell voltage	V	1.9	1.8
LiOH electrolysis	Cathode overpotential	V	0.5	0.3
	Anode overpotential	V	0.3	0.3
	Selectivity	%	90	100
	Cell voltage	V	3.6	3.4

Table S10. Summary of costs for oxygen removal, distillation column, condensation, heating, and compression unit. Related to Figure 3A.

	Scenario	Capital expenses (\$)	Depreciable capital cost (\$)	Electrical power (kW)	Coolant (\$/h)	Heating energy (kJ/h)
Oxygen removal	All	3924860	1647600	53.07	16.6	-1.87E+07*
Distillation	one-step e-NH ₃ RT	2,894,110	793,000	52.32	4.48	4.12E+07
	two-step e-NH ₃ RT					
	three-step e-NH ₃	4,276,480	610,800	147.92	24.70	0
Condensation (NH ₃)	one-step e-NH ₃ RT	1,765,710	166,000	52.32	0.94	N/A
	two-step e-NH ₃ RT					
	one-step e-NH ₃ HT	1,775,570	175,700	52.32	0.93	N/A
	two-step e-NH ₃ HT					
Heating	one-step e-NH ₃ HT	2,472,429	N/A	(7440)	N/A	2.68E+07
	two-step e-NH ₃ HT	648,016	N/A	(1897)	N/A	1.77E+06
O ₂ compression	All	10436100	4316400	1473.08	N/A	N/A
H ₂ compression	(When e-NH ₃ FE<85%)	11342100	6736800	327.59	N/A	N/A

*negative number indicates heat can be recovered from this process

Table S11. The number of processing steps involved in each NH₃ synthesis route. Related to Figure 3B.

	ASU	Oxygen removal	NH ₃ electrolyzer	H ₂ O electrolyzer	Heating	PSA	Distillation	H-B reactors	Condensation	O ₂ compression
<i>Stage 2</i>	10	0	0	1	0	0	0	8	0	8
one-step e-NH ₃ RT	0	10	1	0	0	2	3	0	1	8
one-step e-NH ₃ HT	0	10	2	0	1	4	0	0	1	8
two-step e-NH ₃ RT	0	10	1	1	0	2	3	0	1	8
two-step e-NH ₃ HT	0	10	2	1	1	4	0	0	1	8
three-step e-NH ₃	0	10	1	0	0	0	4	0	1	8

Table S12. Summary of capital costs (million \$). Related to Figure 3A.

	ASU	Oxygen Removal	PEM H ₂ O electrolyzer installed system	NH ₃ electrolyzer installed system	PSA	Distillation	Heating	Condensation	NH ₃ synthesis reactors	O ₂ compression	CCS	Total
Current	0	0	0	0	0	0	0	0	70.00	0	0	70.00
Stage 1	0	0	0	0	0	0	0	0	70.00	0	62.61	132.61
Stage 2	15.30	0	0	0	0	0	0.00	1.770	0.00	10.44	0	63.68
one-step e-NH ₃ RT	0	3.92	0.66	8.46	9.35	2.89	0.00	1.77	0.00	10.44	0	38.03
one-step e-NH ₃ HT	0	3.92	0.66	6.04	13.14	0.00	0.83	1.78	0.00	10.44	0	37.30
two-step e-NH ₃ RT	0	3.92	10.43	8.46	9.35	2.89	0.00	1.77	0.00	10.44	0	47.97
two-step e-NH ₃ HT	0	3.92	10.43	6.04	13.14	0.00	0.00	1.78	0.00	10.44	0	46.41
three-step e-NH ₃	0	3.92	1.75	7.49*	0.00	4.28	0.00	1.77	0.00	10.44	0	28.27

*LiOH electrolyzer cost

Table S13. Summary of operating costs (million \$/year). Related to Figure 3B.

	ASU	Oxygen Removal	PEM H ₂ O electrolyzer installed system	NH ₃ electrolyzer installed system	Heating	PSA	Distillation	Raw materials	Condensation	NH ₃ synthesis reactors	O ₂ compression	CCS	Total
Current	0	0	0	0	0	0	0	6.06	0	3.57	0	0	9.63
Stage 1	0	0	0	0	0	0	0	6.06	0	3.57	0	0.88	10.50
Stage 2	3.04	0.00	6.28	0	0.00	0.00	0.00	0.08	0.00	1.60	0.25	0	11.24
one-step e-NH ₃ RT	0	0.99	0.50	6.80	0.00	0.55	1.45	0.09	0.10	0.00	0.92	0	11.40
one-step e-NH ₃ HT	0	0.82	0.50	6.92	0.25	0.95	0.00	0.09	0.10	0.00	0.90	0	10.28
two-step e-NH ₃ RT	0	0.85	6.70	1.88	0.00	0.55	1.45	0.08	0.10	0.00	0.93	0	12.53
two-step e-NH ₃ HT	0	0.97	6.69	2.01	0.00	0.95	0.00	0.08	0.10	0.00	0.91	0	11.71
three-step e-NH ₃	0	0.87	1.19	11.87	0.00	0.00	0.58	0.16	0.10	0.00	0.94	0	15.71

Table S14. Value ranges for sensitivity analysis for Stage 2 and Stage 3 pathways. Related to Figure 4A.

Sensitivity parameters		Optimistic	Base	Conservative
Electricity price	\$/kWh	0.02	0.03	0.04
NH ₃ selling price	\$/ton	+20%	530	-20%
Selectivity	%	90	70	50
NH ₃ cell cathode over potential	V	0.3	0.5	0.7
NH ₃ electrolyzer stack price	\$/m ²	1000	2000	3000
H ₂ O electrolyzer stack price	\$/m ²	7700	13000	15000
Current density	A/cm ²	0.5 (RT)	0.3 (RT)	0.1 (RT)
		0.7 (HT)	0.5 (HT)	0.3 (HT)
Single-pass conversion	%	25	15	5
Capacity factor		1.0	0.9	0.8

Table S15. Economic performance at different operating loads. Related to Figure 4B.

	Partial load (50%)@3 cents/kWh	Nominal load@3 cents/kWh	Overload (150%)@3 cents/kWh	Overload (150%) @0 cents/kWh
Voltage (V)	1.9	2.1	2.2	2.2
BoP energy losses (kWh/kg)	1.2	1.7	2.1	2.1
Production rate (ton/day)	50	100	150	150
Current density (A/cm ²)	0.5	1.0	1.5	1.5
Capex (million \$)	33.71	33.71	33.71	33.71
Opex (million \$/year)	8.87	13.60	18.72	4.18
LCOA (\$/ton)	625	381	305	28

Table S16. Detailed stream data for ASU (only required for Stage 2) as obtained from Aspen. Related to Figure 5A.

	Unit	Air	1	2	3	4	5	6	7	8	9	9-01
Vapour Fraction		1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	1.00	1.00
Temperature	K	303	565	283	103	103	103	95	95	109	90	173
Pressure	kPa	101	608	608	608	608	608	486	486	527	223	223
Molar Flow	kgmole/h	545	545	545	545	273	273	106	137	30	106	106
Mass Flow	kg/h	15788	15788	15788	15788	7894	7894	2997	3949	949	2997	2997
Liquid Volume Flow	m ³ /h	18	18	18	18	9	9	4	5	1	4	4
		10	10-1	11	12	13	14	15	16	Oxygen	Nitrogen	
Vapour Fraction		0.09	1.00	1.00	1.00	0.10	0.00	1.00	1.00	1.00	1.00	
Temperature	K	98	173	97	77	86	88	91	86	406	298	
Pressure	kPa	233	233	233	101	213	243	243	101	243	101	
Molar Flow	kgmole/h	30	30	273	125	137	420	420	125	420	125	
Mass Flow	kg/h	949	949	7894	3496	3949	12292	12292	3496	12292	3496	
Liquid Volume Flow	m ³ /h	1	1	9	4	5	14	14	4	14	4	

Table S17. Detailed stream data for oxygen removal unit as obtained from Aspen. Related to Figure 5A.

	Unit	Air	Hydrogen-01	Steam/N2-1	liquid	1	2	Hydrogen-02	5-1	6	3	H2O-1
Vapour Fraction		1	1	1	0	1	1	1	1	1	1	0
Temperature	C	25	25	776	776	776	50	25	767	50	50	50
Pressure	kPa	152	152	152	152	152	152	152	152	152	152	152
Molar Flow	kgmole/h	157	16	165	0	165	165	16	170	170	162	3
Mass Flow	kg/h	4537	33	4570	0	4570	4570	33	4547	4547	4515	55
Liquid Volume Flow	m ³ /h	5	0	5	0	5	5	0	5	5	5	0
		Steam/N2-2	5	7	H2O-2	Hydrogen-03	Steam/N2-3	9	10	11	Steam/N2-4	
Vapour Fraction		1	0	1	0	1	1	0	1	1	1	1
Temperature	C	767	767	50	50	25	804	804	804	20	20	20
Pressure	kPa	152	152	152	152	152	152	152	152	152	152	152
Molar Flow	kgmole/h	170	0	153	17	16	161	0	161	161	134	134
Mass Flow	kg/h	4547	0	4241	306	33	4274	0	4274	4274	3793	3793
Liquid Volume Flow	m ³ /h	5	0	5	0	0	5	0	5	5	5	5
Vapour Fraction		H2O-3	Hydrogen-04	13	14	15	16	17	H2O-4	10-1	15-1	
Temperature	C	0	1	1	0	1	1	1	0	1	1	1
Pressure	kPa	20	25	883	883	883	1	1	1	500	400	400
Molar Flow	kgmole/h	152	152	152	152	152	152	152	152	152	152	152
Mass Flow	kg/h	27	16	142	0	142	142	125	18	161	142	142
Liquid Volume Flow	m ³ /h	481	33	3826	0	3826	3826	3505	321	4274	3826	3826
Vapour Fraction		0	0	5	0	5	5	4	0	5	5	5

Table S18. Summary of energy consumption. Numbers are shown in kWh/kg produced NH₃. Related to Figure 5A.

	ASU	Oxygen removal	Electrolyzer	Heating	PSA	Distillation	NH ₃ synthesis reactors	Condensation	O ₂ compression	CCS	Q ₁	Q ₂	Total
Current	0	0	0	0	0	0	11.75	0	0	0	N/A	N/A	11.75
Stage 1	0	0	0	0	0	0	11.75	0	0	0.17*	N/A	N/A	11.92
Stage 2	0.34	0	9.67	0	0	0	0.64	0.01	0.35	0	N/A	0.99	11.00
one-step e-NH ₃ RT	0	0.01	11.82	0	0.55	1.65	0	0.01	0.35	0	N/A	2.58	14.41
one-step e-NH ₃ HT	0	0.01	11.99	0.63	0.89	0	0	0.01	0.35	0	0.63	1.90	13.89
two-step e-NH ₃ RT	0	0.01	13.37	0	0.55	1.65	0	0.01	0.35	0	N/A	2.58	15.95
two-step e-NH ₃ HT	0	0.01	13.53	0	0.89	0	0	0.01	0.35	0	0	1.27	14.80
three-step e-NH ₃	0	0.01	19.06	0	0	0.04	0	0.01	0.35	0	N/A	0.41	19.47

* Number was taken from reference²

Table S19. Electricity CO₂ emissions factor from various sources.³ Related to Figure 5B.

	Electricity sources	gCO _{2e} /kWh
Non-renewable	Nuclear	29
	Natural gas	410
Renewable	Solar/Wind	85
	Geothermal	100
	Hydropower	26
	Other (biomass, etc.)	50

Supplementary Methods

Reaction voltage calculation

Here, we calculated the enthalpy change of reaction from¹:

$$\Delta H_{reaction} = \sum v_i(\Delta H_{products}) - \sum v_i(\Delta H_{reactants}) \quad (1)$$

So the enthalpies of reactants and products can be calculated from heat capacity at constant pressure (C_p)¹:

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad (2)$$

While heat capacity data for components can be calculated by (Table S1)¹:

$$\frac{C_p}{R} = A + BT + CT^2 + DT^{-2} + ET^3 \text{ with } T \text{ in } [K] \quad (3)$$

Then the Gibbs free energy for reactions can be calculated from enthalpy and entropy¹:

$$G_i \equiv H_i - TS_i \quad (4)$$

From the entropy data (listed in Table S2), the reaction voltage can be calculated from the following equation⁴:

$$\Delta G = -nFE_{rxn} \quad (5)$$

n =number of electrons transferred, F =Faradaic constant (96485 C/mole) E_{rxn} =reaction voltage

The results are listed in Table S3 and Figure S1, then enthalpy for NH_3 synthesis reaction:

$$\Delta H^\circ = \frac{1530511.93\text{J}}{4 \text{ mole}} \text{NH}_3 = \frac{382628\text{J}}{\text{mole}} \text{NH}_3 = \frac{22.47\text{MJ}}{\text{kg}} \text{NH}_3$$

Air separation unit calculation

The production rate of NH_3 is set as 100 ton/day (i.e., 5872 kmole/day or 244.67 kmole/hour). Based on material balance, the required N_2 is 2936 kmole/day (122 kmole/h). We designed a cryogenic air separation (Figure S2) process model using Aspen HYSYS based on traditional Linde double-column gas separation systems to meet the purity requirement of N_2 for NH_3 synthesis in Stage 2.⁵ First, air was compressed to 6 atm, cooled to 100 K, and separated before it entered the High Pressure Column (HPC). The rising vapor in HPC which is enriched with N_2 served as reflux for the Low Pressure Column (LPC). Subsequently, the N_2 stream was used to cool the inlet air before it exits the process (Table S16).

Oxygen removal unit calculation

For Stage 3 pathways, we have designed a oxygen removal unit, wherein we used H_2 to burn O_2 in air to produce N_2 . Based on material balance, the required N_2 is 2936 kmole/day (122 kmole/h), along with 787 kmole O_2 which requires 1575 kmole H_2 to react with. We designed a series of Gibbs reactors and coolers (Figure S3) using Aspen HYSYS to combust H_2/O_2 and meet the purity requirement of N_2 for NH_3 electrosynthesis (Table S17).

Process and cost model for distillation (for one-step, two-step, and three-step e- NH_3)

Electrochemical NH_3 synthesis has been demonstrated both in acidic (i.e., HCl) or alkaline electrolyte (i.e., KOH). We thus designed two separate process models to separate dissolved NH_3 from aqueous alkaline and acidic electrolyte (at 1M concentration) in Aspen HYSYS. For separation from acidic electrolyte, a PSA unit is required for separating NH_3 and HCl after the distillation. We then estimated the capital and operating costs for the distillation process using Aspen Economic Analyzer. The PSA cost was calculated from the flow rate of the gases (13.1 m^3/h for NH_3 and 2.9 m^3/h for HCl) on a \$1990000/1000 $\text{m}^3 \text{ h}^{-1}$ basis, which was gathered from a biogas upgrading plant (sample calculation can be found in later parts).⁶ Subsequently, we compared capital and operating costs for these two process models, and presented in Table S4.

The capital cost for NH₃ separation from acidic electrolyte (i.e. HCl) is slightly higher than that from alkaline electrolyte, which is attributed to the addition cost to separate HCl from produced NH₃ using PSA. The operating cost for NH₃ separation from acidic electrolyte is ~1.7 times higher than that from KOH and is attributed to the significant energy required for the reboilers. Therefore, we conclude that the use of KOH as the electrolyte is economically preferable over acid-based electrolytes for electrochemical NH₃ synthesis (Figure S4, Table S4, and Table S5).

For the three-step e-NH₃ process, the last step i.e., hydrolysis reaction of Li₃N is highly exothermic ($\Delta H = -581.62$ kJ/mole Li₃N). In principal, stoichiometric water can be added in this reaction, which will produce LiOH and NH₃. However, in this case, the reaction temperature can reach over 2000 °C, which is far beyond the decomposition (450 °C) and boiling points (924 °C) of NH₃ and LiOH, respectively. Therefore, excess to stoichiometric amount of water needs to be added to maintain the temperature below 450 °C. To reach a final temperature of 450 °C in the reactor, the molar ratio of H₂O: Li₃N needs to be approximately 14.5:1 (see Note below). This ratio will ensure minimum recycling of unreacted water (11.5 mol per mol of NH₃). In this case, the reaction products are a 450 °C vapor mixture (11.5:1 molar ratio of H₂O: NH₃) and molten LiOH salt at 450 °C. Subsequently, we have designed a distillation column to separate NH₃ from H₂O (11.5:1 molar ratio of H₂O: NH₃) using the Aspen Hysys simulation software and achieved 99.34% NH₃ purity.

On the other hand, one might consider reducing the temperature below 450 °C by adding >14.5 mol H₂O per mol of Li₃N. This will lead to lower NH₃ concentration in water, large recycle of unreacted water (>11.5 mol per mol of NH₃), and therefore, may incur higher downstream separation cost. Additionally, this will lower the temperature of produced LiOH below 450 °C, leading to further heating requirement to raise the temperature to 427 °C for LiOH electrolysis in step 1. Therefore, additional cost for NH₃ separation and LiOH heating requirement make this approach not economically compelling.

All parameters are summarized in Figure S14 and Table S6 in Supplemental information.

Note: The consumption of 1 mol of Li₃N releases 581 kJ of heat, which can be used to convert 11.5 mole of liquid water at 25 °C to water vapor at 450 °C. We assumed heat capacity of liquid water is 75.33 J/(mol.K), heat of vaporization of water 44011 J/mol, heat capacity of water vapor 34 J/(mol.K).

Process and cost model for condensation (for one-step, two-step, and three-step e-NH₃)

We first compared the costs of compression and cooling techniques for the condensation model. Compression was found to be more expensive than using coolant for condensation. We designed a condensation unit to make NH₃ suitable for storage and transportation in the Aspen HYSYS process modeling software.⁷ Using propane as refrigerant in the NH₃ condensation process, the NH₃ was cooled from 15°C to -35°C and liquefied at 0.9 atm (Figure S6). Related parameters were gathered from Aspen HYSYS simulation and summarized in Table S7.

Process and cost model for heating (for one-step e-NH₃ HT, and two-step e-NH₃ HT)

We simulated the heating process and to obtain the heat needed to increase the temperature (Figure S7). The cost of heating equipment was calculated from simulation (Heating energy in Table S10) and then estimated for an electric resistance heater.⁸ All costs and energies mentioned in this section are gathered from Aspen HYSYS Economic Analyzer (V10.0).⁹

Process and cost model for O₂ and H₂ Compression (for one-step e-NH₃ HT, and two-step e-NH₃ HT)

In our analysis, we have considered the revenues that can be gathered from side-product O₂ and H₂. The capital and operating cost associated with the compression of H₂ and O₂ were estimated to calculate the LCOA.

We summarized all Aspen related parameters in Table S10.

Mass and material balance

Here, we have shown an example calculation for NH₃ electrosynthesis using N₂ and H₂O at room temperature (Stage 3, one-step e-NH₃ at room temperature). Here, all calculations are performed under the long-term prediction (Table S9).

In the experimental design, we assumed a flow cell configuration for NH₃ electrosynthesis with an electrolyte flow rate of 0.5 ml/min from a similar CO₂ electrolyzer set up.¹⁰ The single-pass concentration of NH₃ (at 0.5 A/cm² current density and 100% FE) in KOH is¹¹:

$$\text{Concentration (NH}_3\text{)} = \frac{0.5\text{A/cm}^2}{3e^-} * \frac{60\text{s}}{96485\text{C}} * \frac{17.03\text{g}}{\text{mole}} \div \frac{0.5\text{mL}}{\text{min}} * 100\% = 0.353 \text{ wt\%/cm}^2$$

As calculated, the concentration of dissolved NH₃ would be too low to be separated economically. Here we assumed that the electrolyte will be recirculated until it reaches 10 wt. % before directing to the distillation unit.

Assuming a 100 ton/day production rate, the current required (i.e., partial current) is:

$$I_{used} = 100000kg * \frac{1000g}{kg} \div \frac{3600s}{hour} \div \frac{24hour}{day} \div \frac{17.03g}{mole} * 3e^- * \frac{96485C}{mole} = 1.97 * 10^7 A$$

The total current under the optimistic conditions:

$$I_{total} = \frac{1.97 * 10^7 A}{90\%} = 2.19 * 10^7 A$$

The electrolyzer power requirement equals the product of the total current, I_{total} , and cell voltage. The cell voltage consists of thermodynamic potential (1.17 V) and overpotential (we assumed 0.3 V cathode overpotential and 0.3 V anode overpotential from state-of-art OER¹²⁻¹⁵):

$$P = V * I = 1.77 V * 2.19 * 10^7 A = 38.69 MW$$

From the total needed current, we calculate the electrolyzer area based on the assumed current density:

$$Area = \frac{21857986.63 A}{0.5 A/cm^2} \div \frac{10000 cm^2}{m^2} = 4371.60 m^2$$

A recycle system was considered to bring back unreacted N₂, so the amount of required N₂ is fixed for 100 ton NH₃ production per day. Therefore, we calculated the amount of daily required N₂ from total current:

$$N_{2(reacted)} = 2.19 * 10^7 A * \frac{1}{6 \frac{e^-}{mole N_2} * \frac{96485C}{mole}} * \frac{28.01g}{mole} * \frac{86400s}{day} = 82.24 ton/day$$

In the optimistic case, we assumed a single-pass conversion of 25%. Thus, the total required N₂ is:

$$N_{2(inlet)} = N_{2(reacted)} \div 25\% = 328.95 ton/day$$

Then unreacted N₂ can be calculated:

$$N_{2(unreacted)} = N_{2(inlet)} - N_{2(reacted)} = 246.71 ton/day$$

This unreacted N₂ was subsequently separated from H₂ and NH₃ and recycled. According to the material balance, the amount of O₂ in the N₂ stream is calculated using their weight concentrations (75.52 wt. % for N₂ and 23.14 wt. % for O₂):

$$O_{2(inlet)} = \frac{82.24ton}{day} \div 75.52\% * 23.14\% = 25.20 \frac{ton}{day} = 787.44kmole/day$$

Then we can calculate the required amount of H₂ to completely remove O₂:

$$H_{2(needed)} = \frac{787.44kmole}{day} * 2 = 1574.89 \frac{kmole}{day} = 3.15 ton/day$$

At the cathode of the electrolyzer, not all electrons flow to reduce N₂ to produce NH₃, hence the flow rate of H₂ produced by the HER side reaction:

$$H_{2(side-product)} = 2.19 * 10^7 A * (1 - 90\%) * \frac{1}{2e^- * \frac{96485C}{mole}} * \frac{2g}{mole} * \frac{86400s}{day} = 1.96 ton/day$$

This indicates an extra H₂O electrolyzer is needed to supply H₂.

$$H_{2(extra)} = 3.15 \frac{ton}{day} - 1.96 \frac{ton}{day} = 1.19 \frac{ton}{day}$$

And the O₂ produced can be calculated from mass balance:

$$O_{2 produced} = m_{H_2O} - m_{H_2,produced} = 176159.72 \frac{kg}{day} - 1957.33 \frac{kg}{day} = 174.20 \frac{ton}{day}$$

Therefore, the H₂O required for anode side to provide protons is:

$$H_2O_{required} = 2.19 * 10^7 A * 2 * \frac{1}{4e^- * \frac{96485C}{mole}} * \frac{18g}{mole} * \frac{86400s}{day} = 176.16 \frac{ton}{day}$$

As a result, we calculate the total gas flow to the PSA unit:

$$V_{total} = V_{NH_3} + V_{N_2} + V_{H_2} = 0 + 246.71 \frac{ton}{day} \div \frac{1.25kg}{m^3} + 1.96 \frac{ton}{day} \div \frac{0.09kg}{m^3} = \frac{2.19 * 10^5 m^3}{day} = 9.13 * 10^3 \frac{m^3}{hour}$$

Estimation of capital and operating cost

Capital cost

Here we have shown a capital cost analysis for ammonia synthesis from N₂ and H₂O at room temperature (one-step e-NH₃ at room temperature) under long-term assumptions. The reference alkaline electrolyzer operates at 1.75 V and 175 mA/cm², and the cost of electrolyzer stack is considered to be ~\$1000 per meter square.¹⁶ Thus, the stack cost of the electrolyzer system:

$$NH_3 \text{ Electrolyzer stack cost} = 4371.60 m^2 * \frac{\$1000}{m^2} = \$4371597$$

Here, we also considered a balance of plant (BoP) cost, which is assumed to be 55% of the electrolyzer stack cost. Eric et al. reported up to 60% reduction in BoP cost for large scale alkaline H₂O electrolyzers due to economics of scale for all major subsystems.^{17,18} As a result, BoP can be calculated as:

$$Balance \ of \ plant = 0.4 * NH_3 \text{ electrolyzer stack cost} * \frac{0.55}{0.45} = \$2137225$$

A 15% contingency factor is added due to the low maturity and associated uncertainty with NH₃ electrolyzers, along with other indirect capital cost (insurance, design, permit, etc. considered as 15% of total cell cost).^{19,20} Therefore, total installed electrolyzer system cost is:

$$\begin{aligned} \text{Total Stage 3 one-step e-NH}_3 @ RT \text{ electrolyzer system cost} \\ = (NH_3 \text{ Electrolyzer cost} + Balance \ of \ plant) * \text{contingency factor} + \text{other indirect capital cost} \end{aligned}$$

For synthesis using H₂ as feedstock (Stage 3 and two-step e-NH₃), we considered 1.8 V and 3.0 A/cm² for PEM water electrolyzer with a \$7700/m² stack cost under long-term prediction.²¹ Based on material balance (every mole of N₂ needs three moles of H₂ to synthesize NH₃), the amount of required H₂ is 8808 kmole/day. Hence, the total current for the H₂O electrolyzer is:

$$I_{total} = 1.97 * 10^7 A$$

The power requirement for H₂O electrolyzer is:

$$P_{total} = 1.97 * 10^7 A * 1.8V = 35.41 MW$$

H₂O electrolyzer cost:

$$H_2O \text{ electrolyzer area} = \frac{1.97 * 10^7 A}{3.0 A/cm^2} \div \frac{10000cm^2}{m^2} = 655.74 m^2$$

$$H_2O \text{ electrolyzer cost} = 655.74 m^2 * \frac{\$7700}{m^2} = \$5049194$$

Similar balance of plant calculation can be applied here:

$$Balance \ of \ plant = 0.4 * H_2O \text{ electrolyzer cost} * \frac{0.55}{0.45} = \$2777057$$

Same contingency factor and indirect cost (used above in NH₃ electrolyzer capital cost calculation) are also needed for H₂O electrolyzers:

$$\begin{aligned} Total \ Stage \ 2 \ H_2O \text{ electrolyzer system capital cost} \\ = (H_2O \text{ Electrolyzer stack cost} + Balance \ of \ plant) * contingency \ factor \\ + other \ indirect \ capital \ cost \end{aligned}$$

Since, H₂ is also needed for O₂ removal, an extra amount of H₂O electrolyzer cost is required:

$$P_{(extra \ H_2)} = \frac{\frac{1.19ton}{day} * \frac{1000kg}{ton} * \frac{1000g}{kg}}{\frac{3600s}{hour} * \frac{24hour}{day}} * \frac{mole}{2g} * \frac{2e^-}{mole} * \frac{96485C}{mole} * 1.8V = 2.40 \text{ MW}$$

Then the size of H₂O electrolyzer can be calculated, as well as the operating cost for this extra amount of H₂.

In room temperature one-step e-NH₃ process, distillation and PSA units are used to separate liquid and gaseous products, respectively (Figure S10). We estimated the total capital cost (direct and indirect) of the PSA process to be based on a 0.7 scaling factor from a biogas upgrading plant, at 1000 m³/h flow rate and 0.25 kWh/m³ energy consumption⁶:

$$PSA \ Capital \ cost = \$1990000 * \left(\frac{9.13 * 10^3 \frac{m^3}{hour}}{1000 \frac{m^3}{hour}} \right)^{0.7} = \$9353415$$

For high-temperature (HT) electrosynthesis (Stage 3, one-step e-NH₃ HT, and two-step e-NH₃ HT), we have estimated the future cost from SOEC (\$228/kW at 0.7 A/cm²), and electric resistance heater is used to elevate the temperature of the inlet streams to 500 °C. The capital cost of the electric heater is estimated based on a reference cost of \$77000/MW from an all-electric H₂ production plant, with a 4.1 installation factor and 5% heat loss from roof and sidewalls.^{8,22}

For NH₃ electrosynthesis using N₂ and H₂O at 500°C, the electric heater cost is:

$$Capital \ cost \ of \ electric \ heater = \frac{\$77000}{MW} * \frac{MW}{1000kW} * \frac{7440kW}{0.95} * 4.1 = \$2472429$$

For SMR-HB plant as we assumed in Current stage and Stage 1, the capital cost was estimated from literature reports for small-scale SMR-HB plant using capital intensity²³:

$$SMR - HB \ reactor \ cost = \frac{\$2000}{ton} * \frac{350days}{year} * 100tons/day = \$70000000$$

The capital investment for Carbon Capture and Storage (CCS) process was calculated from a NGCC plant with CCS.²⁴

The capital cost of the HB reactor (in Stage 2) was estimated using six-tenth rule from an offshore wind-powered ammonia plant with 300 ton/day production rate^{17,25}:

$$HB \ reactor \ cost = (\$53420000) * \left(\frac{100}{300} \right)^{0.6}$$

In the Li-mediated route (three-step e-NH₃), based on a materials balance, 8808 kmole of LiOH is needed (every one mole of NH₃ needs 1.5 moles of LiOH). As LiOH will be recycled after each run in a batch process, we assumed a one-time cost for LiOH. Currently, LiOH market price is around \$20-30/kg, so we consider LiOH cost is \$25/kg and the total cost is²⁶:

$$\text{Cost of LiOH} = \frac{\$25}{\text{ton}} * 8808 \text{ kmole} * \frac{24\text{g}}{\text{mole}} = \$5284800$$

The cost of LiOH was added as part of the NH₃ electrolyzer cost to three-step e-NH₃ process. We estimated the cost for LiOH electrolysis cell using aluminum smelter (\$10.16/ton produced aluminum, crucible furnaces) as representative model due to their similarity in cell configuration. We chose consumable inert anodes (\$128/ton produced aluminum) instead of carbon anodes to avoid CO₂ emission, and the anodes are replaced every three years^{27,28}:

$$\begin{aligned} \text{Capital cost of LiOH cell} &= 8808 \text{ kmole} * \frac{7\text{g}}{\text{mole}} * \left(\frac{\$10.16}{\text{ton}}\right) = \$626 \\ \text{Anode cost for LiOH cell} &= 8808 \text{ kmole/day} * \frac{7\text{g}}{\text{mole}} * \left(\frac{\$128}{\text{ton}}\right) = \$7892/\text{day} \end{aligned}$$

Besides, we also considered the land cost for each of the scenarios considered. Here, the land cost was taken as \$123497/km² with a land factor of three,²⁹ so the total land cost is:

$$\text{Land cost} = \$123497 * 3 = \$370491$$

All capital costs are summarized in Table S12.

Operating cost

The NH₃ electrolyzer's electricity cost is calculated based on the total power requirement:

$$\text{Electricity cost} = 38.69 \text{ MW} * \frac{1000 \text{ kW}}{\text{MW}} * 24\text{hour} * \frac{\$0.02}{\text{kWh}} * \frac{350 \text{ days}}{\text{year}} = \$6499691/\text{year}$$

Electricity cost for the H₂O electrolyzer (to supply extra H₂ in O₂ removal) is calculated based on the total power requirement:

$$\text{Electricity cost} = 2.40 \text{ MW} * \frac{1000 \text{ kW}}{\text{MW}} * 24\text{hour} * \frac{\$0.02}{\text{kWh}} * \frac{350 \text{ days}}{\text{year}} = \$403200/\text{year}$$

Accounting for the heat recovered from O₂ removal process in Stage 3 pathways, the electricity cost for heating the high-temperature (HT) one-step e-NH₃ process is:

$$\text{Heating cost} = \frac{7.44 \text{ MW} - 5.19\text{MW}}{0.95} * \frac{1000 \text{ kW}}{\text{MW}} * \frac{24\text{hour}}{\text{day}} * \frac{350\text{days}}{\text{year}} * \frac{\$0.02}{\text{kWh}} = \frac{\$443012}{\text{year}}$$

Annual maintenance costs are assumed to be 2.5% of the electrolyzers' total installed system cost (sum of stack cost, BoP, contingency, and indirect cost)³⁰:

$$\text{Maintenance cost} = \text{Total cell cost} * 2.5\% = \$9280914 * 2.5\% = \$232023/\text{year}$$

To estimate the operating cost of the PSA unit, a linear scaling calculation was used (at \$0.02/kWh electricity price):

$$\text{PSA operating cost} = 9129.89 \frac{\text{m}^3}{\text{hour}} * 0.25 \text{ kWh} * 24\text{hour} * \frac{\$0.02}{\text{kWh}} * \frac{350\text{days}}{\text{year}} = \$383456/\text{year}$$

The operating cost for the distillation column is the sum of electricity, coolant, and heating energy costs. We converted the heating energy to electricity for the sake of simplicity (Table S10):

$$W_{\text{heating}} = \frac{Q}{t} = \frac{41160000\text{kJ}/\text{h}}{3600\text{s}/\text{h}} = 11433.33 \text{ kW} = 11.43 \text{ MW}$$

Therefore:

Distillation operating cost

$$= (W_{heating} + W_{pump} + W_{Oxygen\ removal}) * \frac{24\text{hour}}{\text{day}} * \frac{350\text{day}}{\text{year}} * \$0.02/\text{kWh} + \frac{\$4.48}{\text{hour}} * \frac{24\text{hour}}{\text{day}} * \frac{350\text{day}}{\text{year}}$$

$$= \$1195623/\text{year}$$

For the condensation (Electrical power and coolant cost in Table S10):

$$\text{Condensation operating cost} = W_{pump} * \frac{24\text{hour}}{\text{day}} * \frac{350\text{day}}{\text{year}} * \$0.02/\text{kWh} + \frac{\$0.93}{\text{hour}} * \frac{24\text{hour}}{\text{day}} * \frac{350\text{day}}{\text{year}} = \$16602/\text{year}$$

Cost of H₂O is³⁰:

$$H_2O\ cost = \frac{176.16\ \text{ton}}{\text{day}} * \frac{\$0.0054}{\text{gal}} \div \frac{3.79\ \text{kg}}{\text{gal}} * 350\ \text{days/year} = \$87551/\text{year}$$

SMR-HB plants are widely constructed all over the world, the cost of natural gas used in SMR-HB (for *Current stage* and *Stage 1*) is calculated from a conventional plant³¹:

$$CH_4\ cost = \frac{100\ \text{ton/day}}{\text{day}} * \frac{\$173}{\text{ton}} * 350\ \text{days/year} = \$6055000/\text{year}$$

The operating cost for a SMR-HB plant includes operating and maintenance (O&M) costs and electricity³¹:

$$O\&M\ cost = \frac{100\ \text{ton/day}}{\text{day}} * \frac{\$42}{\text{ton}} * 350\ \text{days/year} = \$1470000/\text{year}$$

$$\text{electricity cost} = \frac{100\ \text{ton/day}}{\text{day}} * \frac{\$60}{\text{ton}} * 350\ \text{days/year} = \$2100000/\text{year}$$

The operating cost for the HB reactor (Stage 2) is mainly from the compression power and thermal requirement to heat the materials to target pressure and temperature of 150 bar and 450 °C, respectively. This is calculated by linearly scaling down from a similar plant¹⁷:

$$W = \frac{8.02\ \text{MW}}{3} = 2.67\ \text{MW}$$

$$HB\ Reactor\ operating\ cost = 2.67\ \text{MW} * \frac{1000\ \text{kWh}}{\text{MW}} * \frac{24\ \text{hour}}{\text{day}} * \frac{350\ \text{day}}{\text{year}} * \$0.02/\text{kWh} = \$448560/\text{year}$$

We calculated the operating labor cost using the following equation¹⁷:

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5}$$

Where: N_{OL} is the number of operators per shift (3 shifts a day), P is the number of processing steps that include solid handling (0 for our cases), and N_{np} is the number of non-particulate processing steps, including compressors, towers, heat exchangers, reactors and heaters, etc. (summarized in Table S11), and can be calculated in following equation¹⁷:

$$N_{np} = \sum \text{equipment}$$

Hence, the number of operators for each scenario can be calculated using above equations and Table S11, then the operating labor cost can be calculated with salary rate²⁹ :

$$\begin{aligned} \text{Operating labor cost} &= N_{OL} * \text{salary rate} * \text{operating hours} * \text{annual working days} \\ &= 10 * \frac{\$25}{\text{hour}} * \frac{24\text{hours}}{\text{day}} * \frac{350\text{days}}{\text{year}} = \$2186100/\text{year} \end{aligned}$$

We breakdown the labor cost based on the operators required for each process and added them to the processes. The operating cost for each process is summarized in Table S13.

We summarized the distillation cost for room-temperature one-step e-NH₃, both capital and operating, in Figure S15 to show the distribution of each related part.

According to the Aspen manual, both direct and indirect capital costs associated with each process is taken into account to calculate the total capital investment. The direct costs calculated in the Aspen Economic Analyzer (AEA) include: purchased equipment and BoP. Additionally, AEA takes into account other indirect costs, including general and administration (G & A) overhead, contingencies, and contract fees to estimate the total capital investment. In Figure S15 (a), we have provided a breakdown of the total capital investment for the distillation process (the absolute values are shown in Figure 3 in the manuscript) as calculated using AEA.

Similarly, we have considered major variable and fixed operating costs to estimate total operating expense. The major variable operating costs, including utilities, raw materials, maintenance etc. were estimated using AEA as well as process flowsheets and from mass and energy balances. Additionally, we have considered major fixed operating costs, including operating labor costs and plant overhead using AEA. Based on the number of equipment involved in the process, we estimated the number of labor hours and therefore operating labor costs. Figure S15 (b) shows a breakdown of distillation operating costs to illustrate various fixed and variable operating costs considered to estimate the total operating cost (the absolute values are shown in Figure 3 in the manuscript).

Cost analysis for energy storage

In this part, we have compared the costs associated with energy storage to overcome the challenges associated with intermittency of the renewable energy sources. There are two possible ways to overcome the intermittency problem.

Store electricity (e.g., batteries) and run electrolyzer 24/7 to have continuous H₂ production

In this option, we would need to consider the additional costs associated with the electricity storage system. The capital cost of the battery storage system would impact the overall economic feasibility of the process. For example, considering the DOE's projected price of Li-ion battery of \$100/kWh,³² and 25% capacity factor (i.e., solar energy) which means the battery needs to supply electricity for 18 hours:

$$\begin{aligned} \text{Power requirement for } H_2O \text{ electrolyzer} &= 1.8V * 19671683A = 35409938W \\ \text{Battery cost} &= 35409938W \div \frac{1000W}{kW} * 18 \frac{\text{hour}}{\text{day}} * \frac{\$100}{kWh} = \$63737889 \end{aligned}$$

This analysis reveals that the additional cost for the battery system will be over \$60 million. This would double the capital cost of the whole system (Table S12). Assuming today's price of Li-ion (or redox flow battery) of \$469/kWh (or \$858/kWh), the additional capital cost would substantially increase the overall cost of the whole process by over 100%.³³

Operate H₂O electrolyzer partially (e.g., 6 hours/day to adapt with solar energy), and store the produced H₂

In this case, instead of one electrolyzer, we need to consider the capital cost of four electrolyzers, as well as the cost of H₂ storage system:

$$H_2O \text{ electrolyzer cost} = 4 * \frac{19671683A}{\frac{3A}{cm^2}} \div \frac{10000cm^2}{m^2} * \frac{\$7700}{m^2} = \$60588784$$

This indicates that the capital cost of the system would increase significantly, by around 4 times higher compared to the cost without energy storage.

Additionally, this option requires a H₂ storage system. We estimated the cost of an above ground high pressure (~200-300 bar) spherical compressed H₂ tank, which would be the most feasible route. Considering the fact that 17.76 tons of H₂ feedstock is required daily to produce 100 tons of ammonia per day, we estimated the cost of a H₂ storage tank of capacity 176 tons to store 10 days of H₂ feedstock.^{34,35} Following National Renewable Energy Laboratory (NREL) reports on the cost of compression and

storage, we estimated the capital cost of H₂ storage system (i.e., compressor, and storage tank) to be approx. \$0.16 million and occupies approximately 0.3% of the whole plant Capex. From an NREL report, we assumed a capex of H₂ storage tank from the Hydrogen Delivery Scenario Analysis Model (HDSAM) at \$0.9/kg H₂.³⁵ The calculation is as follows:

$$\text{Storage tank cost} = \frac{17.76 \text{ ton}}{\text{day}} * 10 \text{ days} * 1000 \frac{\text{kg}}{\text{ton}} * \$0.9/\text{kg} = 159840\$$$

The cost of the H₂ storage tank occupies approx. 0.3% of the total capex and has been summarized in reactor costs (Table S12).

On the other hand, we estimated the operating cost for H₂ compression assuming ~1.5 kWh/kg H₂ as energy required for compression at electricity price of 2 cents/kWh under the optimistic scenario conditions and a 25% capacity factor i.e., 6 hours of daylight.

$$\text{Storage tank operating cost} = \frac{17.76 \text{ ton}}{\text{day}} * 350 \text{ days} * 18/24 * 1000 \frac{\text{kg}}{\text{ton}} * \frac{1.5 \text{ kWh}}{\text{kg H}_2} * \$0.02/\text{kWh} = 135135\$/\text{year}$$

This operating cost would increase the plant operating cost by 1.5%.

Detailed economic analysis

Here, again, we take room temperature NH₃ synthesis (one-step e-NH₃) as a calculation example.

NPV:

Net Present Value (NPV) = sum of all present values (PV) of the cash flows (CF)³⁶

$$NPV = \sum_{t=1}^n \frac{CF_t}{(1 + NIR)^t} \quad (6)$$

t = year, n = plant life, CF = cash flow, NIR = nominal interest rate

Here, the end-of-life NPV is estimated on a 20-year basis, with a 38.9% tax rate and a 10% nominal interest rate.³⁰ The capital expenses are \$38025600, and the working capital is taken as 5% of capital expenses (\$1901280), while the depreciable capital cost is \$25557329.³⁷ The million dollars difference between capital expenses and depreciable capital cost is that in Aspen Economic Analyzer, direct field costs (equipment rental, insurance, etc.) and indirect costs (taxes, permits, administrative expenses, etc.) are both calculated, indirect costs are not depreciable nor bring benefit in cash flow (see following calculation). In addition, 20% of plant life salvage value is considered. We used a MACRS 10-year depreciation system to recover our capital investment.³⁸

In year 0, the facility is under construction, so the cumulative present value is:

$$\text{Year 0 cumulative present value} = -\$38025600 - \$1901280 = -\$39926880$$

In year 1, produced NH₃ and O₂ brings income:

$$\text{Product income} = \frac{\$530}{\text{ton}} * 1.2 * \frac{100\text{ton}}{\text{day}} * \frac{350\text{day}}{\text{year}} + \frac{0.096\$}{\text{kg}} * \frac{174202\text{kg}}{\text{day}} * 350\text{days}/\text{year} = \$28113200/\text{year}$$

Then income minus operating cost gives us profit:

$$\begin{aligned} \text{year 1 profit} &= \text{Product income} - \text{Operating cost} \\ &= \$28113200 - \$11521518 = \$16591683 \\ \text{year 1 depreciation} &= \$25557329 * 10\% = \$2555733 \\ \text{year 1 profit before tax} &= \text{income} - (\text{operating cost} + \text{depreciation}) = \$14035950 \\ \text{year 1 tax paid} &= \text{profit before tax} * \text{tax rate} = \$5459984 \end{aligned}$$

Therefore:

$$\begin{aligned} \text{year 1 net earning} &= \text{profit before tax} - \text{tax paid} = \$8575965 \\ \text{year 1 cash flow} &= \text{net earning} + \text{depreciation} = \$11131698 \end{aligned}$$

$$\text{year one cash flow(present value)} = \frac{\$11131698}{(1 + 0.1)^1} = \$10119726$$

After 20 years, the cumulative present value is \$54.01M for room-temperature one-step e-NH₃.
Definition of Levelized Cost of Ammonia (LCOA):

$$NPV = 0 = LCOA - \text{Operating Cost PV} - \text{Capital expense} \quad (7)$$

LCOA is calculated when NPV equals zero, which makes it the NH₃ sale price needed for the plant to break even.³⁹

Energy efficiency calculation

Energy efficiency (ϵ) is defined as the ratio of the NH₃ reaction enthalpy (ΔH°) to the total input energy. ΔH° is calculated as 22.5MJ/kg NH₃, and the total energy is the summation of reaction energy for NH₃ electrolyzer (E_1), reaction energy for H₂O electrolyzer (E_2), thermal energy requirement (Q_1), and other required energy (Q_2).⁴⁰

$$\epsilon = \frac{\Delta H}{E_1 + E_2 + Q_1 + Q_2} \times 100\% \quad (8)$$

The required Gibbs free energy is calculated from reaction enthalpies and entropies, and those enthalpies and entropies are gathered and calculated from their physical property data at various temperatures (see Figure S1). Reaction energies for an NH₃ electrolyzer is calculated with varied cathode overpotential:

$$E_1 = (E_1^\circ + \eta_1) * n * F / FE \quad (9)$$

$$E_2 = (E_2^\circ + \eta_2) * n * F / FE \quad (10)$$

Here, E_1° stand for the reaction voltages for NH₃ cell at different temperature (1.17 V for 25°C and 1.20 V for 500°C, showing in Figure S1), E_2° stands for the reaction voltage for H₂O electrolysis at standard conditions (1.23 V). η_1 stands for the overpotential of the NH₃ electrolyzer, while η_2 stands for the overpotential of the H₂O electrolyzer (0.57 V since we choose 1.8 V as the reaction voltage). n is the number of electrons transferred in the reaction (3 e⁻/mole for produced NH₃ and 2 e⁻/mole for produced H₂), F stands for Faradaic constant (96485 C/mole), and FE is the abbreviation for Faradaic Efficiency, which is considered as 90% for NH₃ electrolyzer and 100% for H₂O electrolyzer. All of the data here is summarized in Table S18 and converted to kWh per kg of NH₃. We considered 0.5 kWh/Nm³ for the balance of plant power requirement for both NH₃ and H₂O electrolyzer with a 95% direct current (DC) to alternating current (AC) efficiency.¹⁷

Energy consumption for NH₃ electrolyzer, and the power calculation can be found from above section:

$$W_{NH_3 \text{ electrolyzer}} = (38.69MW * \frac{1000kW}{MW} * 24h \div \frac{100ton}{day} \div \frac{1000kg}{ton} + \frac{0.5kWh}{\frac{Nm^3}{m^3}}) \div 0.95 = 10.50kWh/kg NH_3$$

While the energy consumption for H₂O electrolyzer is:

$$W_{H_2O \text{ electrolyzer}} = \left(1.8V * 19672187.97A \div \frac{1000W}{kW} * 24h \div 100 \frac{ton NH_3}{day} \div 1000kg/ton + \frac{0.5kWh}{\frac{Nm^3}{m^3}} \right) \div 0.95 = 10.27kWh/kg NH_3$$

The same calculation can be applied for other parts and the results are summarized in Table S18.

Cradle-to-gate carbon emission calculation

With the emission factors listed in Table S19, and using the total energy requirement for each process (Table S18), we calculated cradle-to-gate CO₂ emissions (Figure 5B in the manuscript).

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