Supporting Information

Alkaline Ammonia Electrolysis in Membrane Electrode Assembly Cell: Parameter Optimization and Dynamic Operation

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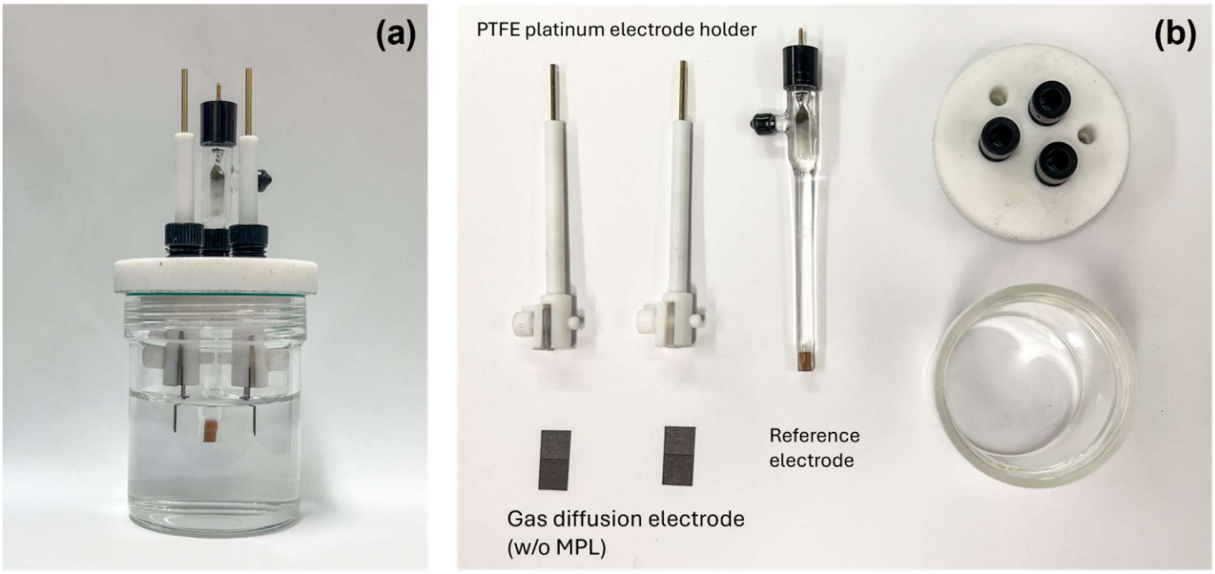


Figure S1. (a) Assembled batch cell. **(b)** Batch cell disassembled parts.

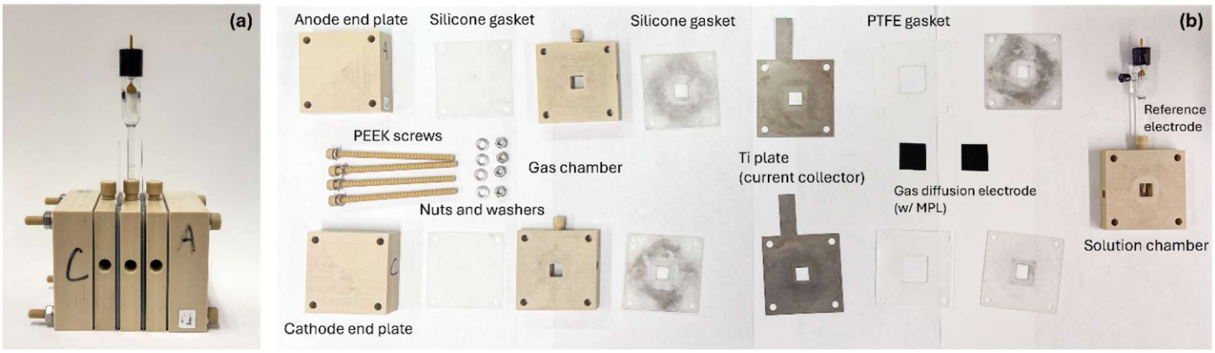


Figure S2. (a) Assembled flow cell. **(b)** Flow cell disassembled parts.

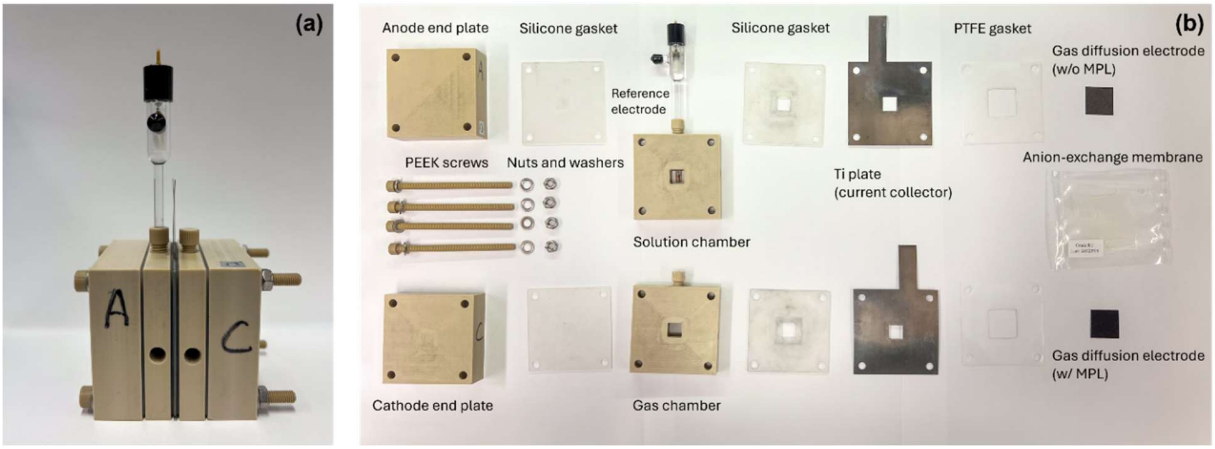


Figure S3. (a) Assembled MEA cell. **(b)** MEA cell disassembled parts.

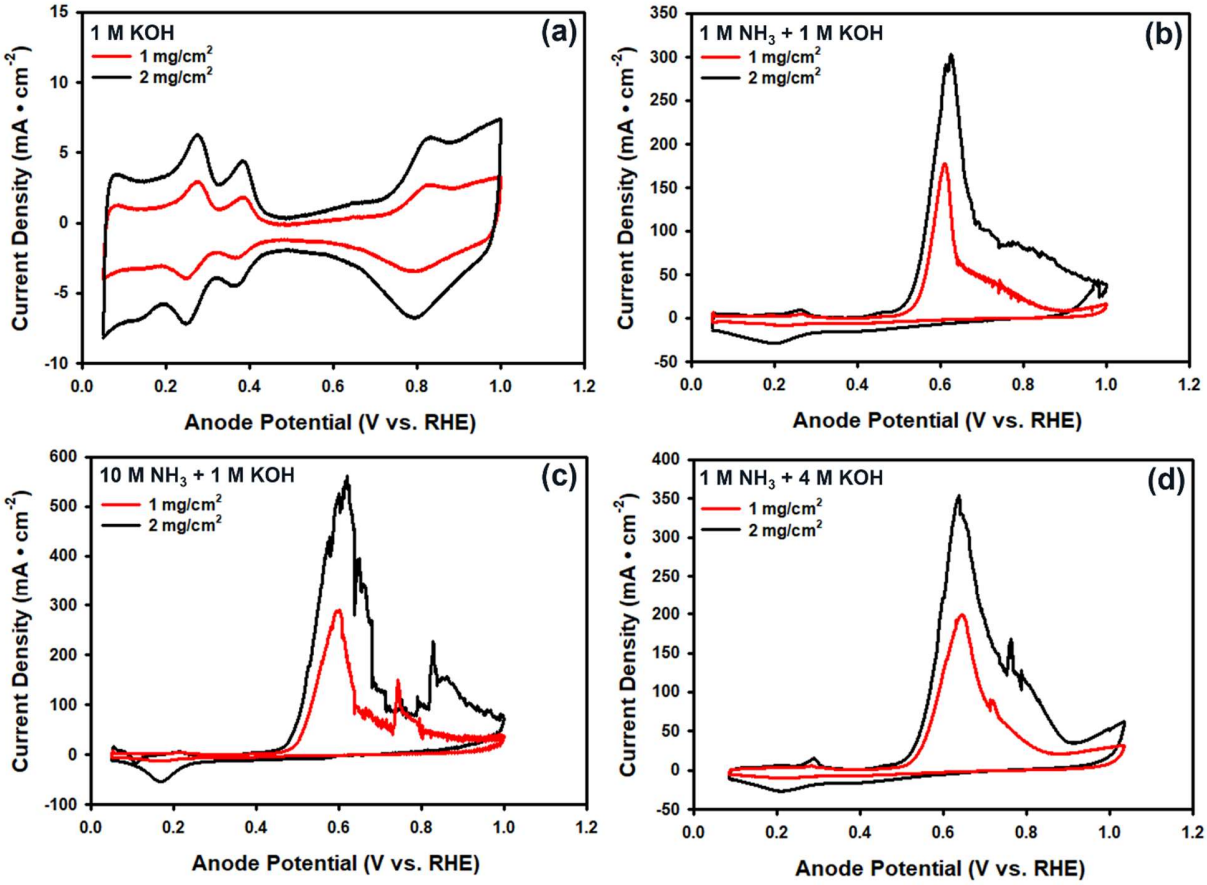


Figure S4. (a) Cyclic voltammetry (5 mV/s) of 1 M KOH at RT using 1 mg/cm^2 and 2 mg/cm^2 Pt. Integrating the area under the H underpotential deposition (UPD) wave and dividing it by the scan rate gives the charge transferred in this region. The electrochemical surface area for each sample was obtained by dividing the charge by 210 μC/cm^2 for adsorbing one monolayer of hydrogen[1, 2]. **(b)** Cyclic Voltammetry (5 mV/s) of 1 M NH_3(aq) and 1 M KOH at RT using 1 mg/cm^2 and 2 mg/cm^2 Pt. **(c)** Cyclic Voltammetry (5 mV/s) of 10 M NH_3(aq) and 1 M KOH at RT using 1 mg/cm^2 and 2 mg/cm^2 Pt. **(d)** Cyclic Voltammetry (5 mV/s) of 1 M NH_3(aq) and 4 M KOH at RT using 1 mg/cm^2 and 2 mg/cm^2 Pt. All flow rates are set to 4 ml/min.

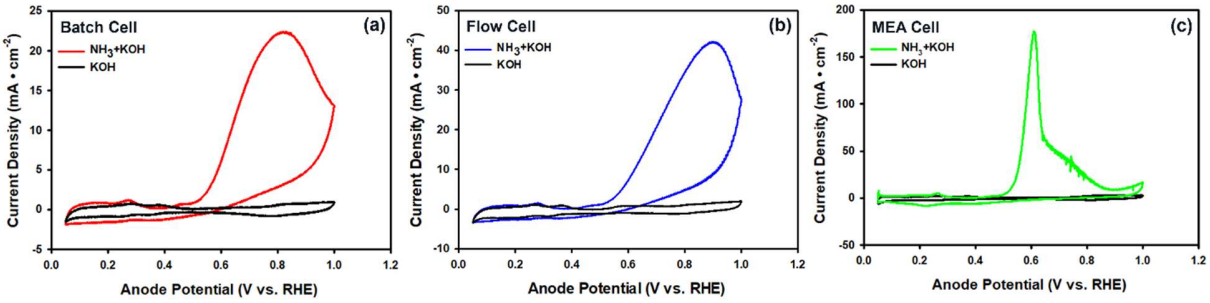


Figure S5. Cyclic Voltammetry (5 mV/s) of the experimental (1 M NH_3 and 1 M KOH) and control groups (1 M KOH) of three cells at room temperature (RT): **(a)** batch cell, **(b)** flow cell, and **(c)** MEA cell. In the flow and MEA cells, solution flow rates are set to 4 ml/min.

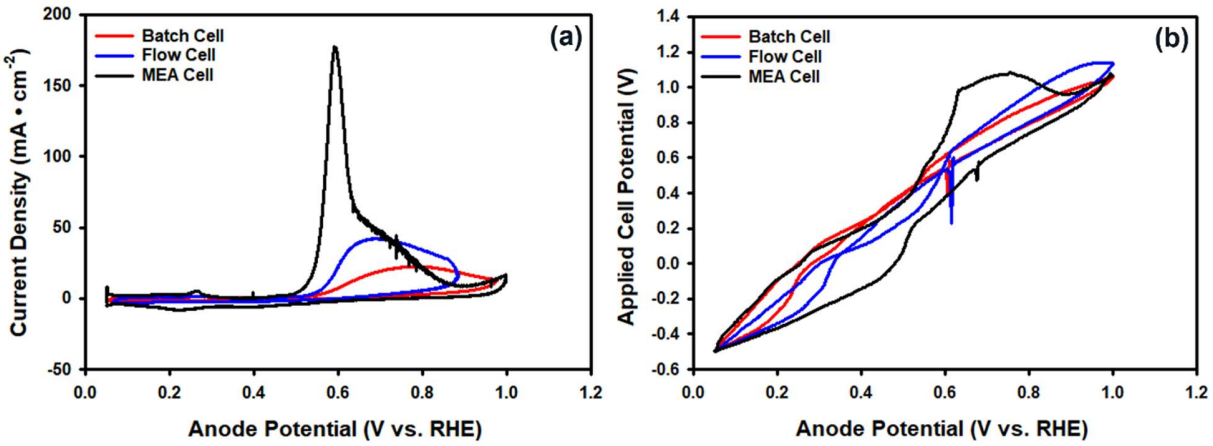


Figure S6. (a) Cyclic Voltammetry (5 mV/s) of 1 M NH_3(aq) and 1 M KOH at RT for the three different cell configurations after iR compensation. **(b)** Plot of applied cell potential vs. anode potential during Cyclic Voltammetry to visualize the range of applied cell potential for AOR. In the flow and MEA cells, solution flow rates are set to 4 ml/min.

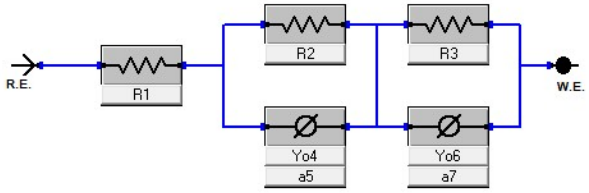


Figure S7. "Two series circuits and solution resistance" equivalent circuit model used to fit the Nyquist plots.

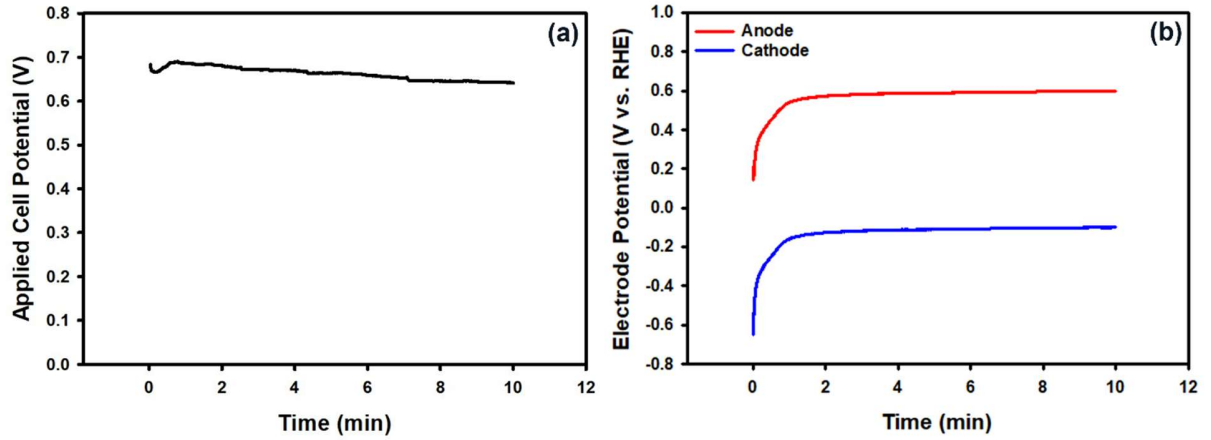


Figure S8. (a) Applied cell potential over time at half-peak anode potential, and **(b)** anode and cathode potentials at applied cell potential of 0.7 V during chronoamperometry with 1 M NH_3(aq) and 1 M KOH at RT. The flow rate is set to 4 ml/min.

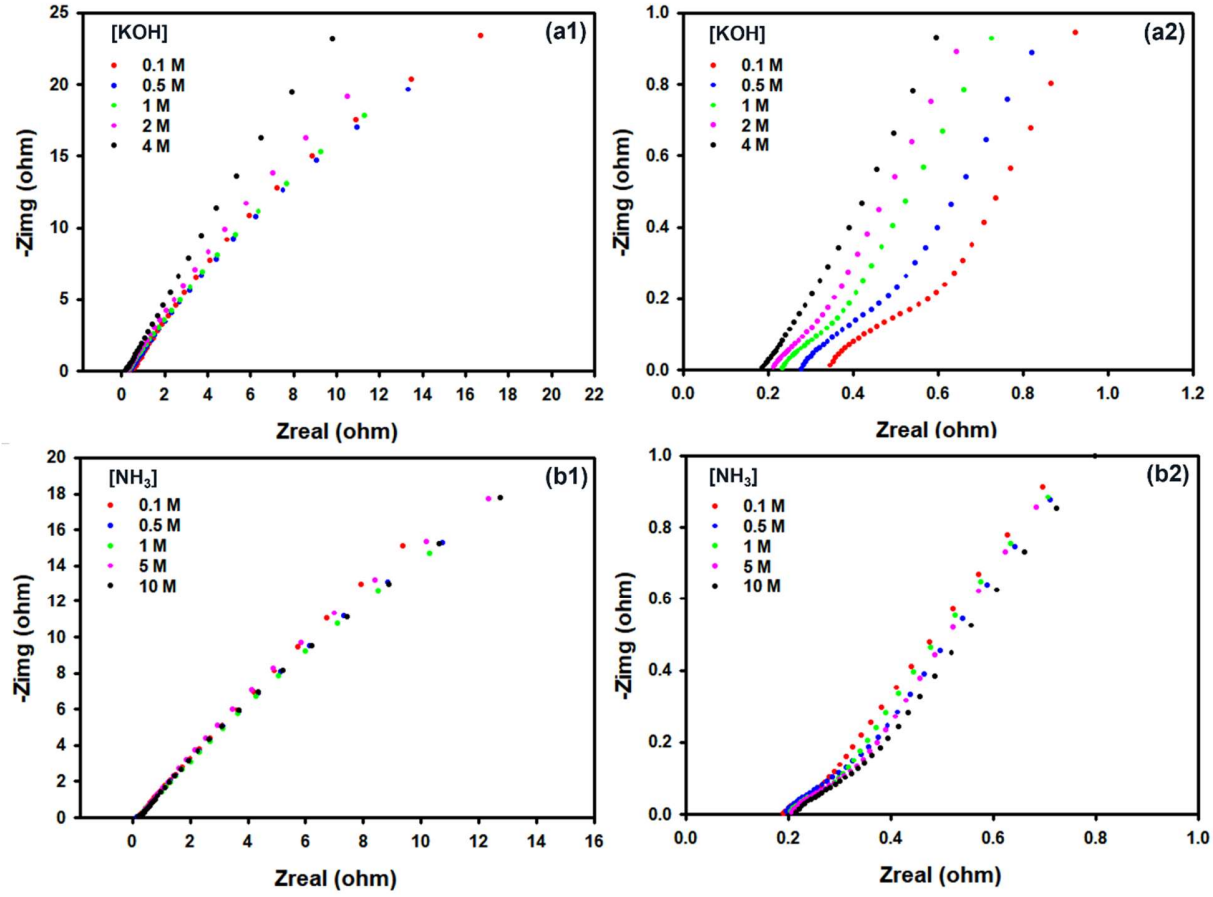


Figure S9. Nyquist plots obtained from potentiostatic EIS measurements of the MEA cell with different KOH concentrations (1 M NH_3(aq)) **(a1, a2)** and with different NH_3 concentrations(1 M KOH) **(b1, b2)**, all measured at open cell potential at RT. **(a1)** and **(b1)** show the whole frequency range, **(a2)** and **(b2)** show the enlarged view of the high frequency region.

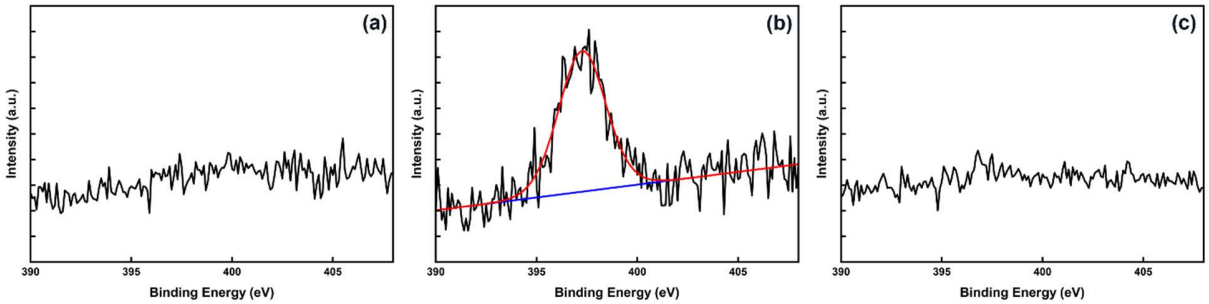


Figure S10. High-resolution N 1s XPS spectra of the MEA anode under three operating conditions: **(a)** before ammonia oxidation (pre-AOR), **(b)** after constant electrolysis, and **(c)** after pulsed electrolysis.

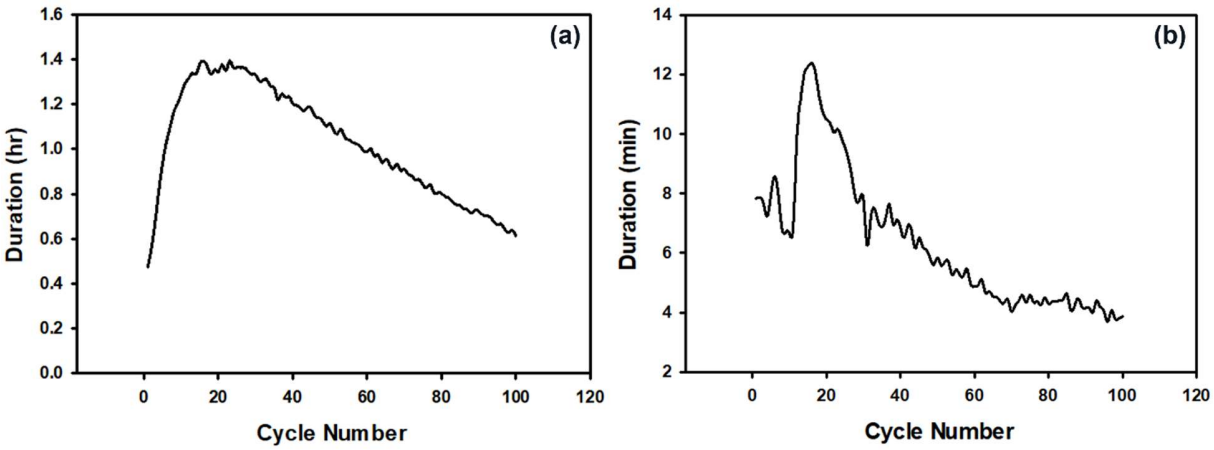


Figure S11. The duration of the working phase with the cycle number: **(a)** 1 min regeneration, 20 mA/cm^2 threshold, **(b)** 1 s regeneration, 60 mA/cm^2 threshold.

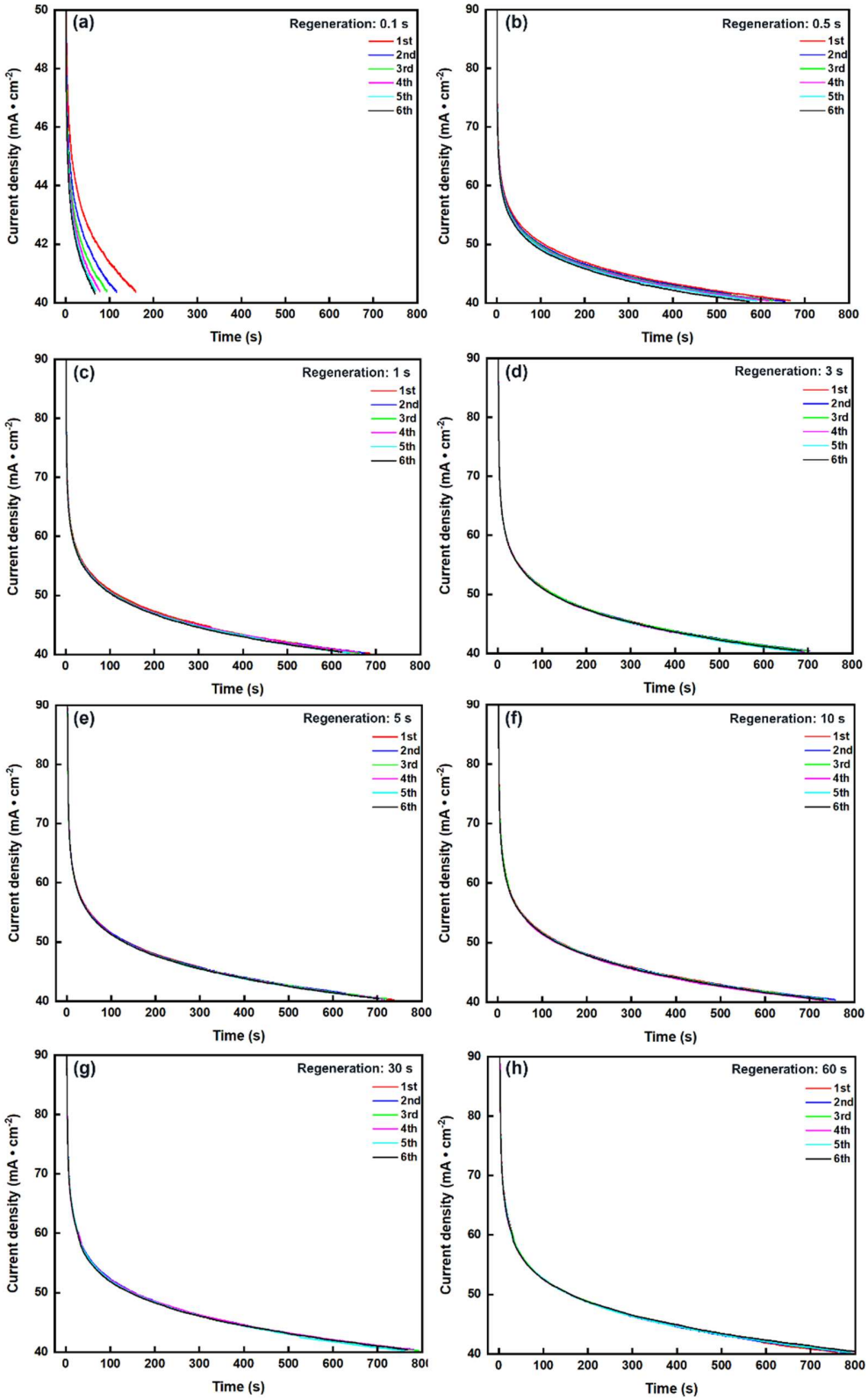


Figure S12. Chronoamperometric profiles of pulsed electrolysis with varying regeneration durations: **(a)** 0.1 s, **(b)** 0.5 s, **(c)** 1 s, and **(d)** 3 s, **(e)** 5 s, **(f)** 10 s, **(g)** 30 s, and **(h)** 60 s. Each condition was tested over six cycles in 10 M NH_3(aq) and 1 M KOH at RT, with a threshold current density of 40 mA/cm^2 during the working phase. The flow rate is set to 4 ml/min.

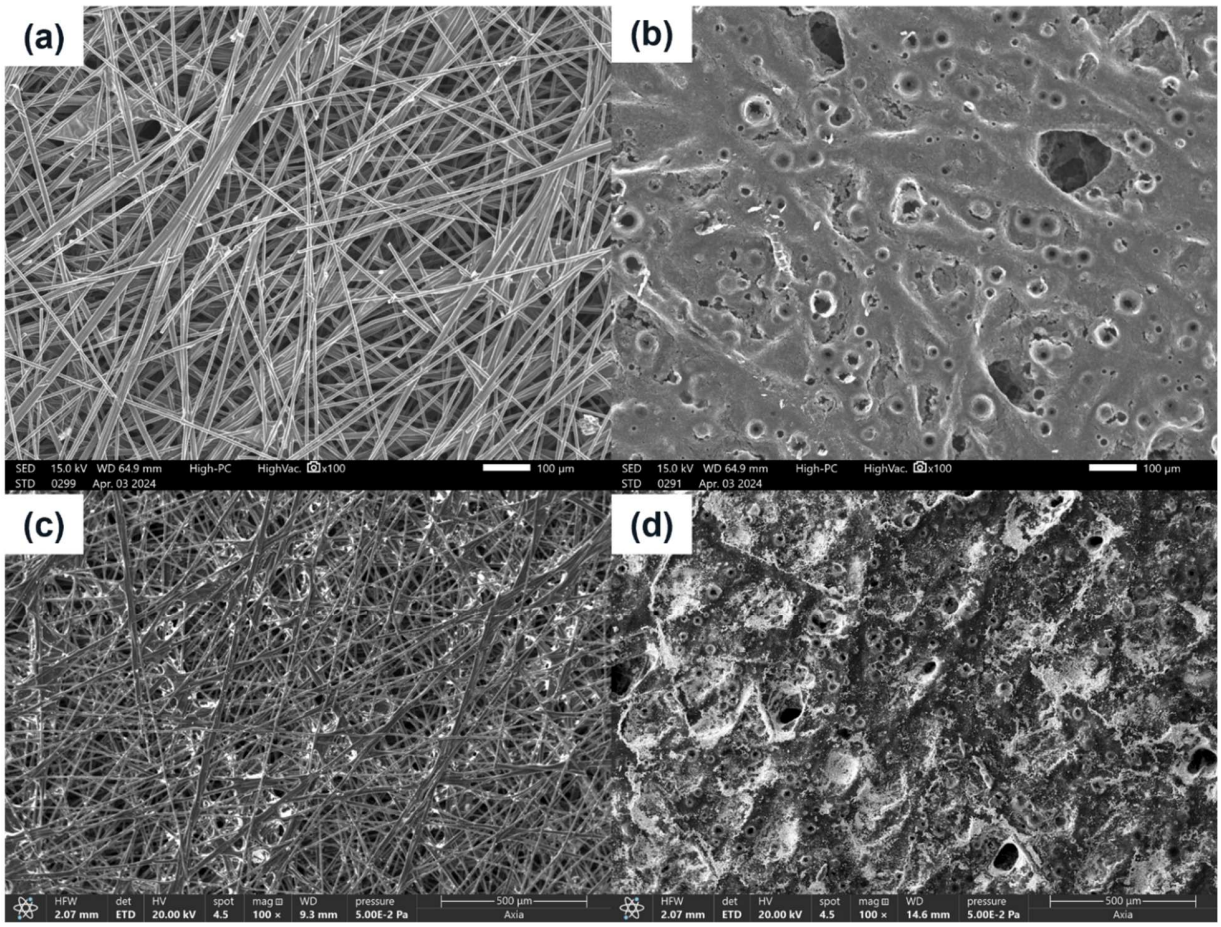
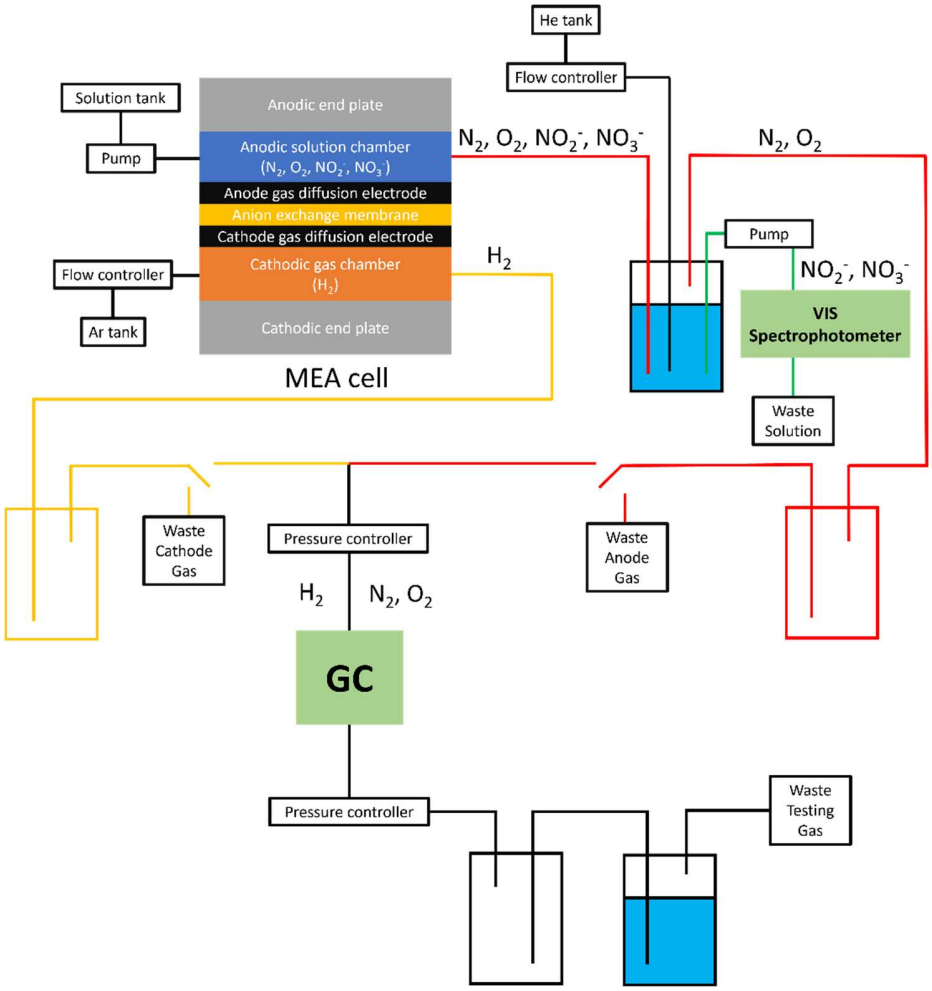


Figure S13. Scanning electron microscope (SEM, JEOL JCM-7000 NeoScope™ Benchtop SEM, T. Schoetz Laboratory and Thermo Fisher Axia ChemiSEM, Material Research Laboratory) graphs of untreated and coated carbon papers (100x magnification): **(a)** untreated AvCarb MGL280, **(b)** coated AvCarb MGL280, (c) untreated AvCarb GDS5130, and d) coated AvCarb GDS5130.



Scheme S1. Schematic diagram illustrating the MEA operation in series with the GC and spectrophotometer analysis for the simultaneous detection of gaseous and ionic products.

Table S1. Fitting results for Electrochemical Impedance Spectroscopy (EIS) of batch, flow, and MEA cell: R1 represents the solution resistance (resistance of the membrane), R2 is the anodic charge transfer resistance, R3 is the cathodic charge transfer resistance, Yo4 is a constant phase element (to model the non-ideal behavior of the EDL) for anode side, and a5 is the exponent associated with Yo4. Similarly, Yo6 is a constant phase element for the cathode side, and a7 is the exponent associated with Yo6.

	R1 (ohm)	R2 (ohm)	R3 (ohm)	Yo4 (S*s^a)	a5	Yo6 (S*s^a)	a7
Batch cell	3.479 ± 0.193	7.167 ± 0.428	4.324 ± 0.223	13.84 ± 0.50 E-3	737.2 ± 31.9 E-3	2.279 ± 0.106 E-3	667.7 ± 26.3 E-3
Flow cell	10.51 ± 0.27	6.506 ± 0.367	90.59 ± 6.38 E-3	45.92 ± 1.83 E-3	633.0 ± 27.0 E-3	6.456 ± 0.255 E-3	1.000 ± 0.000
MEA cell	203.7 ± 17.5 E-3	1.363 ± 0.129	405.9 ± 36.9 E-3	77.73 ± 3.31 E-3	848.0 ± 28.0 E-3	18.28 ± 0.58 E-3	760.8 ± 27.8 E-3

Table S2. Charge information, total time, and average current densities over six cycles with varying regeneration time.

Regeneration time (s)	Working charge per unit area (C/cm^2)	Regeneration charge per unit area (C/cm^2)	Charge ratio (Working: Total)	Total time (min)	Time ratio (Working: Total)	Average current density (mA/cm^2)
0.1	24.66	-35.52	99.9%	9.72	99.9%	42.3
0.5	170.4	-987.2	99.4%	62.2	99.9%	45.6
1	181.7	-178.4E+1	99.0%	65.8	99.8%	46.0
3	192.7	-288.6E+1	98.5%	69.7	99.6%	46.1
5	199.3	-380.6E+1	98.1%	72.1	99.3%	46.1
10	206.9	-581.0E+1	97.3%	75.2	98.7%	45.8
30	218.4	-126.9E+2	94.5%	81.0	96.4%	44.9
60	220.0	-209.3E+2	91.3%	84.3	93.4%	43.5

Table S3. Average current densities, total time, and charge per unit area of working and regeneration phases in long-term testing of 10 M NH_3 and 1 M KOH with pulsed electrolysis at ±0.7 V (1 s regeneration, 60 mA/cm^2 threshold).

	Average current density (mA/cm^2)	Total time (min)	Total charge per unit area (C/cm^2)
Working	68.2	634.9	2.60E+3
Regeneration	-442	1.7	-4.42E+1

Table S4. Summary of Faradaic efficiencies (FEs) under various electrolysis conditions. The table includes results from chronopotentiometry (first and second stages) and pulsed electrolysis (first and second 100-cycle sets), covering N_2, O_2, H_2, NO_3^- Faradaic efficiencies, and NH_3 crossover rates. All results are presented as average values with standard errors (mean ± SE), unless otherwise noted.

Chronopotentiometry:

Table S4a. N_2-FE in chronopotentiometry: first stage.

	N_2%	Carrier gas flow rate (sccm)	Current (mA)	N_2-FE%
First Stage	0.389	50	80	104.8
	0.329	55	80	97.4
	0.323	55	80	95.8
		N_2-FE (mean ± SE)		99.3 ± 2.8%

Table S4b. N_2-FE, O_2-FE and NO_3^--FE in chronopotentiometry: second stage.

	N_2%	Carrier gas flow rate (sccm)	Current (mA)	N_2-FE%
	0.189	20	80	14.8
	0.187	20	80	16.3
	0.187	20	80	15.3
		N_2-FE (mean ± SE)		15.5 ± 0.4%
	O_2%	Carrier gas flow rate (sccm)	Current (mA)	O_2-FE%
Second Stage	0.615	20	80	66.2
	0.614	20	80	66.1
	0.589	20	80	63.5
		O_2-FE (mean ± SE)		65.3 ± 0.9%
	NO_3^- (mg/L)	Solution flow rate (mL/min)	Current (mA)	NO_3^- -FE%
	13.0	4	80	13.5
	13.0	4	80	13.5
	13.1	4	80	13.6
		NO_3^--FE (mean ± SE)		13.5 ± 0.0%

1st 100 Cycles of Pulsed Electrolysis (1 min regeneration, 20 mA/cm^2 threshold):

Table S4c. N_2-FE (anode) and H_2-FE (cathode) from first 100 cycles of pulsed electrolysis (1 min regeneration, 20 mA/cm^2 threshold).

	N_2%	Carrier gas flow rate (sccm)	Current (mA)	N_2-FE%
Anode	0.271	30	34.7	100.7
	0.267	30	34.7	99.2
	0.266	30	34.7	98.8
	0.282	30	34.7	104.9
	0.256	30	34.7	95.3

	N_2-FE (mean ± SE)			99.8 ± 1.6%
	H_2%	Carrier gas flow rate (sccm)	Current (mA)	H_2-FE%
Cathode	1.223	20	34.7	101.2
	1.221	20	34.7	101.0
	1.284	20	34.7	106.2
	1.227	20	34.7	101.4
	0.786	30	34.7	97.5
	H_2-FE (mean ± SE)			101.5 ± 1.4%

Table S4d. NH_3 crossover rates from first 100 cycles of pulsed electrolysis (1 min regeneration, 20 mA/cm^2 threshold).

NH_3%	Carrier gas flow rate (sccm)	NH_3 crossover rate (mmol/min)
4.69	20	0.04188
4.80	20	0.04286
4.60	20	0.04107
4.86	20	0.04339
4.47	20	0.03991
NH_3 crossover rate (mean ± SE)		(4.18 ± 0.06) × 10^{-2}

2nd 100 Cycles of Pulsed Electrolysis (1 s regeneration, 60 mA/cm^2 threshold):

Table S4e. N_2-FE (anode) and H_2-FE (cathode) from second 100 cycles of pulsed electrolysis (1 s regeneration, 60 mA/cm^2 threshold).

	N_2%	Carrier gas flow rate (sccm)	Current (mA)	N_2-FE%
Anode	0.542	30	68.2	102.7
	0.515	30	68.2	97.6
	0.496	30	68.2	94.0
	0.504	30	68.2	95.5
	0.546	30	68.2	103.5
	N_2-FE (mean ± SE)			98.7 ± 1.9%
	H_2%	Carrier gas flow rate (sccm)	Current (mA)	H_2-FE%
Cathode	1.620	30	68.2	102.3
	1.533	30	68.2	96.8
	1.549	30	68.2	97.8
	1.564	30	68.2	98.8
	1.461	30	68.2	92.3
	H_2-FE (mean ± SE)			97.6 ± 1.6%

References

1. S. Rudi, C. Cui, L. Gan and P. Strasser, *Electrocatalysis*, 2014, **5**, 408-418.
2. K. J. J. Mayrhofer, D. Strmcnik, B. B. Blizanac, V. Stamenkovic, M. Arenz and N. M. Markovic, *Electrochim. Acta*, 2008, **53**, 3181-3188.