Supplementary Information

Direct electrolysis of liquid anhydrous ammonia for continuous production of high-purity, pressurized hydrogen at ambient temperature

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Equations of ammonia electro-oxidation reaction (AOR)

Anode:
$$2NH_3(aq) + 6OH^-(aq) \rightarrow N_2 + 6H_2O(1) + 6e^-, E^0 = -0.77 \text{ V vs. SHE}$$
 (Eq. S1)

Cathode:
$$6H_2O(1) + 6e^- \rightarrow 3H_2 + 6OH^-$$
, $E^0 = -0.83$ V vs. SHE (Eq. S2)

Net Reaction:
$$2NH_3(aq) \rightarrow N_2 + 3H_2$$
, $E^0 = 0.06 V$ (Eq. S3)

SHE: Standard Hydrogen Electrode

Calculation of overall cell potential of NH₃(l) electrolysis:

Firstly, we continuously purge Ar during electrolysis using a **semi-batch reactor** with an assumption that NH_3 is completely converted into N_2 and H_2 . The cell potential for $NH_3(l)$ electrolysis is calculated at the pressure of 6.2 bar at 10°C (283.15 K).

Net Reaction:
$$NH_3(1) \rightarrow 1/2N_2 + 3/2H_2$$
 (Eq. S4)

Based on Nernst's equation, the cell potential (E_{cell}) is calculated.

$$E_{cell} = -\frac{\Delta G^{0}}{3F} - \frac{RT}{3F} ln \left(P_{N_{2}}^{\frac{1}{2}} P_{H_{2}}^{\frac{3}{2}} \right)$$
(Eq. S5)

The first term of the standard Gibbs free energy change ($\Delta G^0 = 11.01 \text{ kJ mol}^{-1}$) at Eq. S5 is calculated using the following values with Eqs. S4 and S6:^{1, 2}

$$\Delta G_f^0 = \Delta H_f^0 - T \Delta S_f^0$$
(Eq. S6)
$$\Delta H_f^0 (NH_3(1)) = 67.2 \text{ kJ mol}^{-1},$$
$$\Delta S^0 (NH_3(1)) = 103.3 \text{ J mol}^{-1}, \Delta S^0 (H_2(g)) = 130.7 \text{ J mol}^{-1}, \Delta S^0 (N_2(g)) = 191.6 \text{ J mol}^{-1}$$

Due to the lack of available entropy data under our specific experimental conditions, the E_{cell} at 283 K was estimated using the equation (Eq. S6) based on the ΔH_{f^0} and ΔS_{f^0} values at 298 K reported in previous literature.¹⁻³ As explained,^{3,4} this approach assumes that thermodynamic properties remain approximately constant over small temperature intervals and has been validated in similar systems.

Thus, the first term is
$$-\frac{\Delta G^0}{3F}$$
 is -0.038 V

The second term of the standard Gibbs free energy change at Eq. S5 is calculated using the following values: R is 8.314 J mol⁻¹ K⁻¹; T is 283.15; P_{N2} is the partial pressure of N₂,1.6 bar; P_{H2} is the partial pressure of H₂, 4.6 bar; F is 96,485 C mol⁻¹.

Thus, the second term is 0.021 V.

Finally, the E_{cell} of Eq. S5 in semi-batch reactor is 0.059 V.

In the **full electrolysis cell**, H_2 and N_2 gases are generated separately, allowing the cell potential to be calculated based on the total pressure rather than the individual partial pressures. Accordingly, the corrected cell potential in this case is given as follows: The first term remains constant at -0.038 V, while the second term is calculated based on the partial pressures of N_2 and H_2 , which are measured at 6.2 bar. As a result, the second term yields a value of **0.030** V. Therefore, the corrected cell potential (E_{cell}) for the **flow electrolysis cell**, as described in Eq. S5, is calculated to be **0.068** V.

Calculation of hydrogen evolution reaction (HER) potential in anhydrous NH₃(l)

The potential of the HER at a pressure of H₂ of 4.6 bar at 10°C in a batch reaction system.

Possible HER pathways are:

$$3NH_4^+ + 3e^- \rightarrow 1.5H_2 + 3NH_3(l)$$
$$3NH_4^+ \rightarrow 3NH_3(l) + 3H^+$$
$$3H^+ + 3e^- \rightarrow 1.5H_2(g)$$

Based on Nernst's equation,

$$E_{cell} = E_{cell}^{0} - \frac{RT}{nF} \ln K$$

where, $E_{cell}^{0} = 0$ by definition in the case of standard hydrogen electrode (SHE). We replace the conventional use of a_{H+} with a_{NH4+} , because during the reaction H⁺ is primarily supplied through the dissociation of NH₄⁺, not from freely available H⁺. Note that NH₃(l) is a strong Brønsted base, which implies that meaning that NH₄⁺ has poor H⁺ dissociation property. Accordingly, the concept of pH is replaced by pNH₄⁺, defined as:

$$pNH_4^+ = -log_{10}(a_{NH4+})$$

The Nernst equation for the HER in this system becomes:

$$E = 0 - \frac{RT}{nF} \ln \frac{p_{H2}/p^0}{a_{NH4}^2 + e^2}$$
$$E = -2.303 \frac{RT}{F} (pNH_4^2 + \frac{1}{2} \log \frac{p_{H2}}{p^0})$$

Under reaction conditions, the cell potential is calculated as follows:

$$E = -0.056(pNH_4^+ + 0.33)$$

Due to the lack of experimentally reported data on the activity of NH_4^+ in $NH_3(l)$, concentration was used as an approximate substitute for activity in this calculation.

The pH of NH₃(1) in 1.0 M of NH₄Br,

$$K_{eq} \text{ of } 2NH_3(1) \leftrightarrow [NH_4^+] [NH_2^-] = 10^{-33} (223K)$$

$$pNH_4^+ = \frac{\log \frac{1}{[NH_4^+]}}{[NH_4^+]} = \sim 0$$

Therefore, we consider $pNH_4^+ = 0$, and HER is given as follows: E = -0.018 V

Conversion of reference hydrogen electrode (RHE) to SHE using the Ag/AgCl (3.4 M) reference electrode

We consider pH = 0, following Supplementary Note 2.

For the RHE,

 $E(RHE) = E^{0}(SHE) + 2.303 \frac{RT}{F} pH$ $E(RHE) = E^{0}(SHE)$

Converting the potential of Ag/AgCl (3.4M KCl) to SHE.

 $E(SHE) = E(Ag/AgCl) + E^{0}(Ag/AgCl)$

The referenced study presents results of $E^0(Ag/AgCl)$ at only 25°C and -40°C.⁵ Given that the potential difference between these temperatures is minimal (approximately 59 mV), we have opted to use the data at 25°C for our purposes at our experimental condition (25°C in NH₃(l)).

 $E^{0}(Ag/AgCl)$ at 25°C in NH₃(l) = 622 mV

E(SHE) = 0.622 V + E(Ag/AgCl)

Calculation of Faradaic efficiency (FE) of H₂

$$FE(\%) = \frac{nZF}{Q} \times 100$$

where *n* is the amount of product detected (mol); *Q* is the total passed charge (C); *F* is the Faradaic constant (96,485 C mol⁻¹); *Z* is the number of electrons required to obtain one molecule of H_2 .

Considering H₂ production in 1 min, the applied current is 2.5 A (Q = 150 A), and Z is 2 to generate one molecule of H₂ (Eq. 4).

Finally, the theoretical H₂ production for 1 min is 0.00078 mol.

Converting units from mol to L:

$$V = \frac{nRT}{P}$$

where *n* is 0.00078 mol; *R* is the gas constant (0.082 L atm K⁻¹ mol⁻¹); *T* is 293.15; *P* is 1 atm. Thus, the calculated V is 0.01875 L of H_2 .



Fig. S1 Schematic illustration of the semi-batch reactor for the electrolysis of NH₃(l).

Fig. S1 note

The reactor vessel, thermocouple, level sensor, and agitator are coated with polytetrafluoroethylene (PTFE) to prevent corrosion caused by NH₃.



Fig. S2 HAADF-STEM images and particle size histograms of the M/C (M = Pt, Ru, Pd, Ni, Fe, and Co) catalysts. The calculated average particle sizes are as follows: Pt: 2.1 ± 0.6 nm, Ru = 2.8 ± 1.1 nm, Pd = 3.7 ± 2.0 nm, Ni = 6.5 ± 3.8 nm, Fe = 7.2 ± 4.6 nm, and Co = 15 ± 7.2 nm.

Fig. S2 note

HAADF-STEM: High-angle annular dark-field scanning transmission electron microscopy; M/C: Metal supported on Carbon



Fig. S3 Electrochemical performance of the M/C (M = Pt, Ru, Pd, Ni, Fe and Co) catalysts for the anodic reaction (NER) in 1 M NH₄Br/NH₃(l): (A) overpotentials (η) and (B) Tafel slopes, as calculated from the data in Fig. 2A.

Fig. S3 note

V: Voltage; SHE: Standard Hydrogen Electrode



Fig. S4 XPS N 1s spectra of Ru/C catalyst: (black line) fresh, (red line) 1 h used in $NH_3(l)$ electrolysis with 5 M NH_4Br at 0.1 A cm⁻² and 10°C, 6.2 bar conditions.



Fig. S5 Electrochemical performance of the M/C (M = Pt, Ru, Pd, Ni, Fe and Co) catalysts for the cathodic reaction (HER) in 1 M NH₄Br/NH₃(l): (A) overpotentials (η) and (B) Tafel slopes, as calculated from the data in Fig. 2B.

Fig. S5 note

V: Voltage; SHE: Standard Hydrogen Electrode



Fig. S6 Electrochemical performance of Ru || Ru and Ru || Pt for the anodic reaction (NER): (A) overpotentials (η) and (B) Tafel slopes, as calculated from the data in Fig. 2C.



Fig. S7 Electrochemical performance of Pt \parallel Pt and Ru \parallel Pt for the cathodic reaction (HER): (A) overpotentials (η) and (B) Tafel slopes, as calculated from the data in Fig. 2D.



Fig. S8 Nyquist plots obtained using different electrode configurations with various electrolyte concentrations (1, 5, and 10 M) of NH₄Br, measured over the frequency range from 100 kHz to 100 MHz: (A) anodic reaction (NER) at a baseline potential of +1.0 V vs. SHE and (B) cathodic reaction (HER) at a baseline potential of -1.2 V vs. SHE. The plots are fitted (black line) with an equivalent circuit (inset figure) to estimate charge transfer resistance (R_{ct}).

Fig. S8 note

R_s: Solution resistance; CPE: Constant phase element

	A. NER				B. HER			
	Ru Ru Ru Pt Ru Pt Ru Pt				Ru Pt	Ru Pt	Ru Pt	Ru Pt
	1 M	1 M	5 M	10 M	1 M	1 M	5 M	10 M
$R_{ct}(\Omega)$	6.5	5.1	2.5	2.1	6.7	3.5	3.1	2.6
$R_{s}\left(\Omega ight)$	1.9	1.6	0.8	0.8	1.9	1.6	0.8	0.8

Fitted results are described as below:



Fig. S9 Linear sweep voltammograms with a scan rate of 5 mV s⁻¹ recorded on a Ru \parallel Pt configuration using 5 M NH₄PF₆ and NH₄Br as supporting electrolytes in NH₃(l) at 10°C and 6 bar.



Fig. S10 A zero-gap type $NH_3(l)$ electrolyzer with the electrode area of 25 cm²: (A) Schematic illustration of the components of the as-developed $NH_3(l)$ electrolyzer, and (B) Digital image of the $NH_3(l)$ electrolyzer

Fig. S10 note

The current collectors are coated with Au, and the flow field plates are coated with Pt. The gaskets are made from ethylene propylene diene monomer (EPDM) rubber to prevent corrosion caused by NH₃.



Fig. S11 GC-TCD reference results: (A) N_2 , $NH_3(g)$ peaks obtained using the standard gas and (B) H_2 , N_2 peaks obtained using the standard gas. Online GC-TCD spectra monitored during $NH_3(l)$ electrolysis experiments: (C) N_2 , $NH_3(g)$ and (D) H_2 , N_2 from cathode and (E) N_2 , $NH_3(g)$ and (F) H_2 , N_2 from anode.

Fig. S11 note

GC-TCD: Gas chromatography (GC) with temperature conductivity detector (TCD)

The concentrations of the standard gases used in Figs. S9A and B are as follows:

A: NH₃(g) 50 mol%, N₂ 50 mol%, H₂ 0 mol%

B: NH₃(g) 0 mol%, N₂ 50 mol%, H₂ 50 mol%



Fig. S12 Reusability of the supporting electrolyte (NH₄Br): (black) fresh electrolyte and (red) second-use electrolyte. I–V polarization curves of the as-designed NH₃(l) electrolyzer were measured with a scan rate of 5 mA s⁻¹ at a flow rate of 30 mL min⁻¹ at 10°C and 6.2 bar with 5 M NH₄Br.

Table S1 Inductively coupled plasma optical emission spectrometry (ICP-OES) results of fresh and 1 h used catalysts: Ru/C (anode) and Pt/C (cathode) used in NH₃(l) electrolysis with 5 M NH₄Br at 0.1 A cm⁻² and 10°C, 6.2 bar conditions.

	Ru/C	Pt/C
Fresh	2.5 μmol cm ⁻²	2.5 μmol cm ⁻²
1 h	1.5 μmol cm ⁻²	2.4 μmol cm ⁻²

Anode	Cathode	Electrod e size (cm ²)	Electrolyte	Temp. (°C)	Pressure (bar)	H ₂ Purity	System	Current density @ Potential	Ref.
Pt plate	Pt plate	2	1 M KNH ₂	25	10	<66.7% N ₂ , H ₂ and NH ₃ (g) mixture	Batch (12 mL)	7 mA cm ⁻² @ 2.0 V	4
Pt plate	Pt plate	4	5 M KNH_2	25	9.5	<66.7% N ₂ , H ₂ and NH ₃ (g) mixture	Batch (35 mL)	50 mA cm ⁻² @ 2.0 V	6
Pt disk	Pt disk	-	1 M NH ₄ PF ₆	-70 - 65	1	<66.7% N ₂ , H ₂ and NH ₃ (g) mixture	Batch	170 mA cm ⁻² @ 2.0 V	3
Pt plate	Pt plate	4	5 M NH ₄ Cl	25	10	<66.7% N ₂ , H ₂ and NH ₃ (g) mixture	Batch	13.5 mA cm ⁻² @ 1.5 V	7
Rh–Pt–Ir alloy	Pt-foil	0.5	1 M NH ₄ I	20	8.5	<66.7% N ₂ , H ₂ and NH ₃ (g) mixture	Batch (40 mL)	60.8 mA cm ⁻² @ 2.0 V	8
Rh–Pt–Ir alloy	Pt-foil	0.5	1 M NH ₄ Br	20	8.5	<66.7% N ₂ , H ₂ and NH ₃ (g) mixture	Batch (40 mL)	40.3 mA cm ⁻² @ 2.0 V	8
Fe wire (1 mm)	Pt mesh	-	0.1 M KPF ₆	-70 - 65	1	<66.7% N ₂ , H ₂ and NH ₃ (g) mixture	Batch	38 mA cm ⁻² @ 1.5 V	9
Ru plate	Pt plate	1	0.5 M KNH ₂	25	10	<66.7% N ₂ , H ₂ and NH ₃ (g) mixture	Batch (76 mL)	2 mA cm ⁻² @ 0.5 V	10
Ru/C	Pt/C	25	5 M NH₄Br	10	6.2	>99.99% Only H ₂	Continuous Electrolysis Cell (Zero-gap type)	100 mA cm ⁻² @ 1.1 V 500 mA cm ⁻² @ 1.6 V	This Work

Table S2 Comparison of the regults in th	is study with proviously reports	d NIH (1) alastrolygic Systems
Table 52 . Comparison of the results in th	is study with previously reporte	a $NH_3(1)$ electrolysis Systems.

 Table S3 Comparison of hydrogen production technologies.

	Water Electrolysis	Steam Methane Reforming (SMR)	Solid Oxide Electrolysis Cell (SOEC)	NH ₃ Electrolysis
Temperature	50–80°C	700–1000°C	700–1000°C	0–25°C
H ₂ Source	H ₂ O	$CH_4 + H_2O$	H ₂ O (steam)	Liquid NH ₃
Minimum Voltage	>1.23 V	-	>0.9 V	>0.059 V
Advantages	 no CO₂ emission (if renewables are used) Compact design High purity of H₂ 	 High TRL (Industrial level) Low cost H₂ 	 Low cell potential than water electrolysis High efficiency (when both electricity and heat are utilized) 	 Low cell potential Low operating Temperature High purity, pressurized H₂
Disadvantages	 High E consumption Sensitive to e⁻ costs Safety issue (H₂/O₂ crossover) Distillation cost of H₂O Noble metal catalyst High-cost membrane 	 - CO₂ emission - Low purity of H₂ (need purification) - Centralized system 	 Scalability Material stability issues (mechanically) High quality steam 	Low TRLElectrode stabilitySuitable membrane
Temperature	50–80°C	700–1000°C	700–1000°C	0–25°C

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