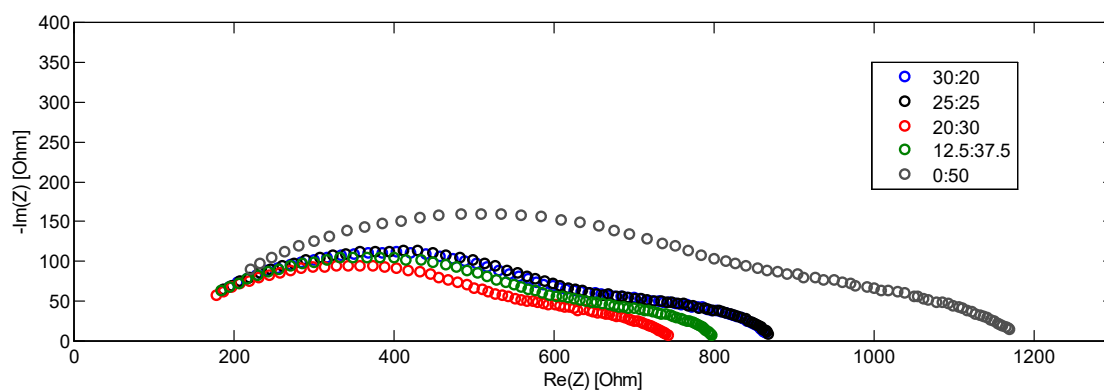


S-1 Electrical characteristics



**Fig.-S 1** Nyquist plots of Fe/BZY-Pt|BZY|Pt. Legend presents various gas ratios of  $N_2$  and  $H_2$ .

**Table-S 1** Impedance fitting results of Fe/BZY-Pt|BZY|Pt in mixed  $N_2$  and  $H_2$

Gas ratio $N_2:H_2$	$R_s$ [ $\Omega$ ]	$R_1$ [ $\Omega$ ]	$CPE_{1-T}$ [ $F \cdot s^{CPE1-P-1}$ ] $\times 10^{-4}$	$CPE_{1-P}$	$R_2$ [ $\Omega$ ]	$CPE_{2-T}$ [ $F \cdot s^{CPE2-P-1}$ ] $\times 10^{-6}$	$CPE_{2-P}$	$f_1$ [Hz]	$f_2$ [Hz] $\times 10^4$
30:20	93.4	263	6.07	0.38 5	530	4.47	0.47 8	18.8	4.99
25:25	93.1	252	5.95	0.38 9	542	4.28	0.47 8	20.7	5.16
20:30	90.6	217	6.84	0.35 7	451	4.76	0.47 6	33.4	6.34
12.5:37.5	92.5	216	6.11	0.38 8	504	4.25	0.47 9	29.4	5.94
0:50	91.7	385	3.84	0.34 9	723	2.85	0.48 7	38.1	5.28

Where

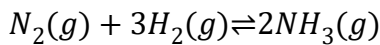
$$\begin{cases} \omega_{max1} = 2\pi f_1 = \frac{1}{C_1 R_1} \\ \omega_{max2} = 2\pi f_2 = \frac{1}{C_2 R_2} \end{cases} \# \quad eq.-S 1$$

$$C = T^{1/P} R^{\frac{1-P}{P}} \# eq.-S 2$$

$$\begin{cases} f_1 = \frac{1}{(T_1 R_1)^{1/P_1} 2\pi} \\ f_2 = \frac{1}{(T_2 R_2)^{1/P_2} 2\pi} \end{cases} \# \quad eq.-S 3$$

## S-2 Thermochemical coefficients and calculation

In this work, the equilibrium constant  $K$  of the  $NH_3$  formation reaction was calculated in the condition of atmospheric pressure and 773.15 K. the calculated  $K$  by van't Hoff equation is  $7.17 \times 10^{-5}$ . With the obtained  $K$ , and equation relating the  $N_2$  conversion rate to the  $N_2$  fraction is given.



$$Cp^\circ = A + Bt + Ct^2 + Dt^3 + E/t^2$$

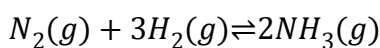
$t = \text{temperature(K)}/1000$

$$\Delta_r H^\circ(T)$$

$$= \Delta_r H^\circ(298.15 \text{ K}) + 2 \int_{298.15 \text{ K}}^T Cp^\circ NH_3 dT - \int_{298.15 \text{ K}}^T Cp^\circ N_2 dT - 3 \int_{298.15 \text{ K}}^T Cp^\circ H_2 dT$$

$$\left( \frac{\partial \ln K}{\partial T} \right)_p = \frac{\Delta_r H^\circ}{RT^2}$$

$$K = \frac{\left( \frac{p_{NH_3}}{p^\circ} \right)^2}{\left( \frac{p_{N_2}}{p^\circ} \right) \left( \frac{p_{H_2}}{p^\circ} \right)^3}$$



Before reaction:

$$T(\text{inlet}) = N_2(\text{inlet}) + H_2(\text{inlet})$$

$$N_2(\text{inlet}) = T(\text{inlet}) \times x(\text{N}_2 \text{ fraction})$$

$$H_2(\text{inlet}) = T(\text{inlet}) \times (1 - x)$$

In equilibrium:

$$NH_3(\text{eq}) = N_2(\text{inlet}) \times y(\text{conversion}) \times 2 = T(\text{inlet}) \times x \times y \times 2$$

$$N_2(\text{eq}) = N_2(\text{inlet}) \times (1 - y) = T(\text{inlet}) \times x \times (1 - y)$$

$$H_2(\text{eq}) = H_2(\text{inlet}) - \frac{3}{2} \times NH_3(\text{eq}) = T(\text{inlet}) \times (1 - x) - 3 \times T(\text{inlet}) \times x \times y$$

$$T(\text{eq}) = N_2(\text{eq}) + H_2(\text{eq}) + NH_3(\text{eq})$$

$$\frac{\left(\frac{pNH_3}{p^\circ}\right)^2}{\left(\frac{pN_2}{p^\circ}\right)\left(\frac{pH_2}{p^\circ}\right)^3} = \frac{(NH_3(\text{eq})/T(\text{eq}))^2}{(N_2(\text{eq})/T(\text{eq}))(H_2(\text{eq})/T(\text{eq}))^3} \frac{2^2 \times y^2 \times \left(\frac{1}{x} - 2y\right)^2}{(1 - y) \times \left(\frac{1}{x} - 1 - 3y\right)^3} = K$$

Figure-S 2 shows the equilibrium  $NH_3$  production rate at 500 °C with different inlet  $N_2$  gas fractions. The total gas flow rate was 50 mL/min (equivalent to  $1.31 \times 10^{-5}$  mol/s). The highest  $NH_3$  production rate is achievable at a  $N_2:H_2$  ratio of 1:3, and  $N_2$  conversion increased as the  $N_2$  fraction decreased. Figure-S 3 shows the mathematical solution derived from the reaction equilibrium calculations, given as:

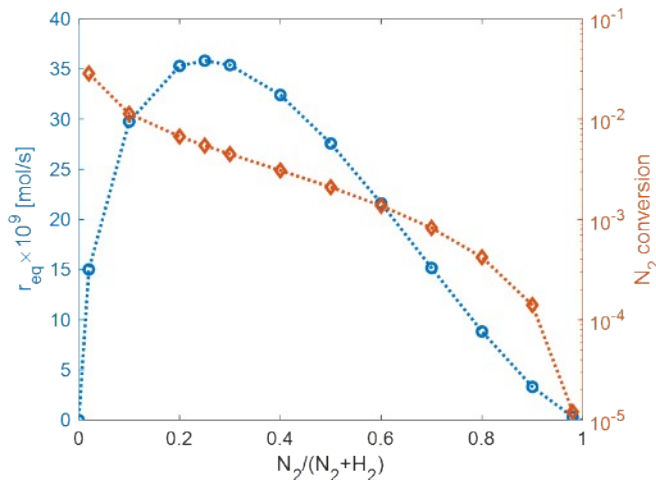
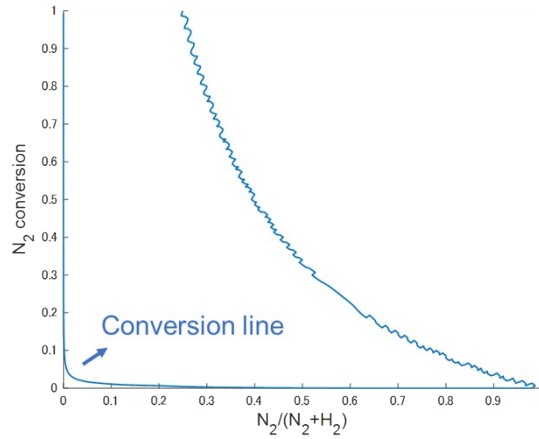


Fig.-S 2 Equilibrium  $NH_3$  production rate ( $r_{eq-NH_3}$ ; calculated using an equilibrium constant of  $7.17 \times 10^{-5}$  at 500 °C) as a function of the  $N_2$  gas fraction (blue). The total inlet gas flow rate was 50 mL/min. The corresponding  $N_2$  conversion (red) is plotted on a semi-logarithmic scale.

$$\frac{2^2 \times y^2 \times \left(\frac{1}{x} - 2y\right)^2}{(1-y) \times \left(\frac{1}{x} - 1 - 3y\right)^3} = K \quad \#eq.-S4$$

where  $x$  and  $y$  stand for  $N_2/(N_2 + H_2)$  and the  $N_2$  conversion ratio, respectively, and  $K$  is the equilibrium constant at 500 °C ( $7.17 \times 10^{-5}$ ). As shown in Fig.-S 3,  $N_2$  conversion increased as the fraction of  $N_2$  decreased.



**Fig.-S 3** Mathematical solution calculated from the reaction equilibrium equation at 500 °C.

**Table-S 2** Coefficients in Shomate equation for  $C_p^\circ$  calculation<sup>1</sup>.

Species (g)	A	B	C	D	E
NH <sub>3</sub>	19.99563	49.77119	-15.37599	1.921168	0.189174
H <sub>2</sub>	33.066178	-11.363417	11.432816	-2.772874	-0.158558
N <sub>2</sub> (100-500K)	28.98641	1.853978	-9.647459	16.63537	0.000117
N <sub>2</sub> (500-2000K)	19.50583	19.88705	-8.598535	1.369784	0.527601

**Table-S 3** Standard enthalpy of formation and standard entropy at 298.15 K<sup>1</sup>

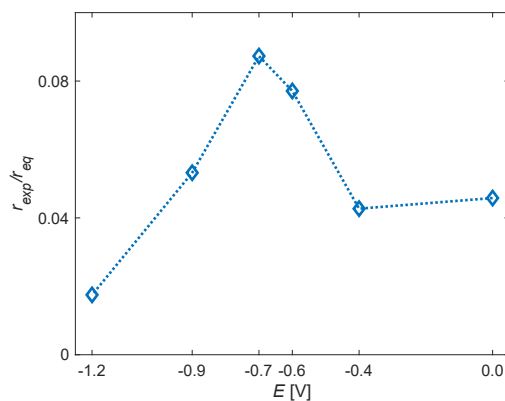
Species (g)	$\Delta_f H^\circ$ [kJ/mol]	$S^\circ$ [J/(mol K)]
NH <sub>3</sub>	-45.90	192.77

H <sub>2</sub>	0	130.68
N <sub>2</sub>	0	191.61

Figure-S 4 shows the ratio between experimental NH<sub>3</sub> production rate ( $r_{\text{exp-NH}_3}$ ) and theoretical equilibrium NH<sub>3</sub> production rate ( $r_{\text{eq-NH}_3}$ ). An equilibrium constant,  $K$ , of  $7.17 \times 10^{-5}$  was calculated for NH<sub>3</sub> production from N<sub>2</sub> and H<sub>2</sub> (the coefficients for  $C_p^\circ$  calculations, standard formation enthalpies, and standard entropies are listed in Table-S 2 and Table-S 3). With a H<sub>2</sub> and N<sub>2</sub> gas flow rate of 25 mL/min (equivalent to  $6.57 \times 10^{-6}$  mol/s) at the inlet, the calculated NH<sub>3</sub> equilibrium production rate ( $r_{\text{eq-NH}_3}$ ) was  $1.38 \times 10^{-8}$  mol/s. Protons pumped from the anode side to the cathode side can cause an increase in the H<sub>2</sub> concentration. The H<sub>2</sub> flow rate at each applied voltage ( $f_{\text{eq-H}_2}$ ) was calculated from the sum of the inlet flow rates of 25 mL/min and the amount of H<sub>2</sub> produced from the protons assuming a current efficiency of 1, as follows:

$$f_{\text{H}_2} = \frac{I}{nF} \quad \#eq.S-5$$

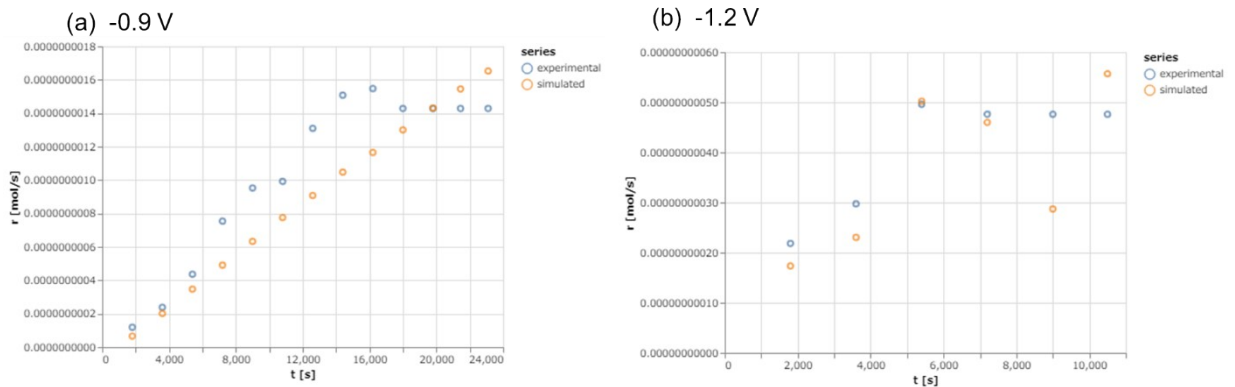
where  $n$  is the moles of electrons consumed for every mole of H<sub>2</sub> produced ( $n = 2$ ), and  $I$  is the current at each applied voltage. As a result, the  $r_{\text{eq-NH}_3}$  values at the applied voltages were slightly higher than  $r_{\text{eq-NH}_3}$  at the OCV, and the experimentally measured NH<sub>3</sub> production rate was lower than the theoretically calculated NH<sub>3</sub> production rate at equilibrium.



**Fig.-S 4 Ratio between experimental NH<sub>3</sub> production rate ( $r_{\text{exp-NH}_3}$ ) and theoretical equilibrium NH<sub>3</sub> production rate ( $r_{\text{eq-NH}_3}$ ) ( $r_{\text{eq-NH}_3}$  at OCV; calculated using an equilibrium constant of  $7.17 \times 10^{-5}$ ).**

### S-3 Fitting results

For  $N_2 + 2 * \xrightarrow{k_1} 2N *$  #eq.1, the reaction rate equation of  $2 \frac{dN^*}{dt} = k_1 [ * ]^2$  and  $2 \frac{dN^*}{dt} = k_1 [ * ]^2 / [H_s]^2$  are also tried for simulation. However, losses calculated by  $\sum_{\text{experimental time}} (\sum [NH_3 \text{ error}]^2 / \sum [NH_3 \text{ experimental}]^2)$  with  $2 \frac{dN^*}{dt} = k_1 [ * ]^2$  and  $2 \frac{dN^*}{dt} = k_1 [ * ]^2 / [H_s]^2$  are quite large. Although the flow rates of  $N_2$  and  $H_2$  are known, the concentrations of  $N_2$  and  $H_2$  on the surface of the catalyst are unknown. Since the flows of  $N_2$  and  $H_2$  are far in excess relative to reaction intermediates and products, the concentrations of  $N_2$  and  $H_2$  are both set to be a constant dimensionless number 1. There are large discrepancies between simulation and experimental data at -0.9 V and -1.2 V in Fig.-S 5.



**Fig.-S 5 Experimental and simulation plots of NH<sub>3</sub> production rate against time at -0.9 V and -1.2 V.**

**Table-S 4 Parameters obtained at -0.9 V and -1.2 V.**

	-0.9 V	-1.2 V
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<b><math>k_1</math> [mol<sup>-1</sup>s<sup>-1</sup>]</b>	6.13×10 <sup>-8</sup>	1.04×10 <sup>-1</sup>
<b><math>k_2</math> [mol<sup>-3</sup>s<sup>-1</sup>]</b>	9.46×10 <sup>-1</sup>	9.46×10 <sup>-1</sup>
<b><math>k_3 \times 10^5</math> [mol<sup>-1</sup>s<sup>-1</sup>]</b>	-	-
<b><math>k_{-3}</math> [mol<sup>-1</sup>s<sup>-1</sup>]</b>	1.21	1.21
<b><math>k_4 \times 10^5</math> [s mol<sup>-2</sup>]</b>	9.71	9.71
<b><math>k_5 \times 10^{-8}</math> [s mol<sup>-2</sup>]</b>	6.54	6.54
<b>* total amount [mol]</b>	3.88×10 <sup>-2</sup>	3.88×10 <sup>-2</sup>
<b>V<sub>H</sub> total amount [mol]</b>	1.71	1.71
<b>N* steady state [mol]</b>	3.83×10 <sup>-2</sup>	3.87×10 <sup>-2</sup>
<b>H<sub>s</sub> steady state [mol]</b>	3.92×10 <sup>-6</sup>	1.85×10 <sup>-6</sup>

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<sup>1</sup> NIST (National Institute of Standards and Technology, U.S. Department of Commerce)  
Chemistry WebBook