Electronic Supplementary Material (ESI) for Materials Advances.

Table S 1 Catalytic NH_3 production rate over a Fe/BZY catalyst at 500 ºC.

CYCLE	1	2	3	4	5	6
Reaction rate [10^{-8} mol/(s·g-cat.)]	6.5	2.3	4.1	2.8	5.7	4.6

The catalytic activity of a Fe/BZY catalyst for NH_3 formation was evaluated at 500 ºC and atmospheric pressure under a feed of N_2 at 10 ml/min and H_2 at 30 ml/min. The Fe/BZY catalyst of 0.19 g was used and the outlet gas was trapped by distilled water in a water trap for 3 min with an interval of 30 min. The amount of ammonia in the distilled water trap was quantified by the salicylate method.

Table S 2 Blank experiment results for NH_3 contamination from the atmosphere and catalytic NH_3 formation from gases leaking between the anode and cathode.

		Collected on cathode side [mol/(s·cm²)]		Collected on anode side [mol/(s·cm²)]	
		NH_3	N_2H_4	NH_3	N_2H_4
Blank	Anode: Ar (20%H_2O)	BLD	BLD	BLD	BLD
exp. 1	Cathode: dry N_2	BLD	BLD	BLD	BLD
Blank	Anode: Ar (20%H_2O)	BLD	BLD	BLD	BLD
exp. 2	Cathode: dry Ar	BLD	BLD	BLD	BLD
Blank	Anode: H_2 (3% H_2O)	BLD	BLD	BLD	BLD
exp. 3	Cathode: dry N_2	BLD	BLD	BLD	BLD

The amounts of NH_3 produced in the blank experiments were all below detection limit. The detection limit for NH_3 is 0.01 mg/L, which corresponds to NH_3 production rate of

2.5x10^{-11} mol/(s sm^2), and that for N_2H_4 is 4 µg/L and the corresponding formation rate is 4.4x10^{-12} mol/(s sm^2).

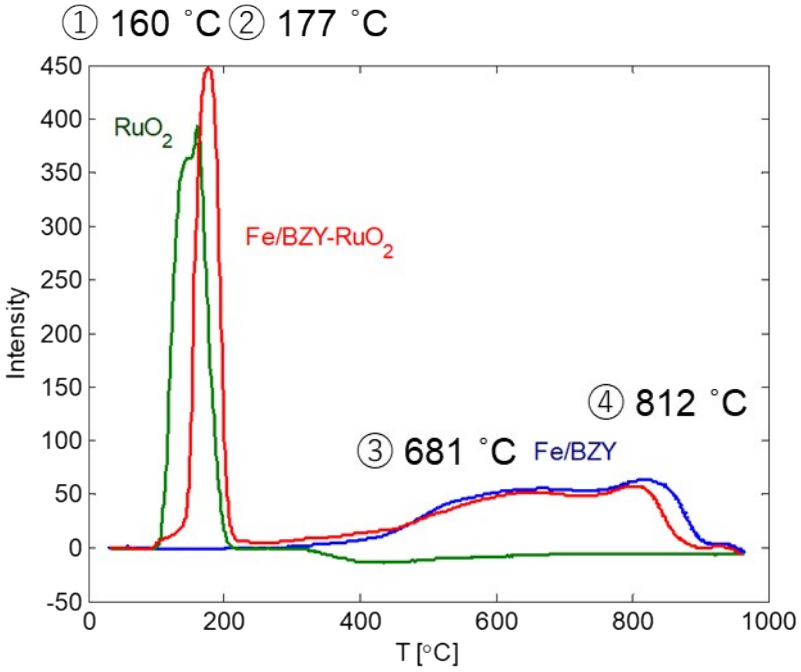

Fig. S 1 TPR profiles of 5 mg RuO_2 (green), 30 mg Fe/BZY (blue), 5 mg RuO_2 and 30 mg Fe/BZY mixture (red). The samples were pretreated at 220 ˚C for 30 min using a heating rate of 10 K/min in Ar with a flow rate of 50 ml/min and cooled to room temperature. After flushing in diluted H_2 (5% H_2 in Ar) with a flow rate of 50 ml/min for 1 h, the samples were heated to 1000 ˚C at a heating rate of 10 K/min

Table S 3 Impedance fitting result under dry N_2.

Applied voltage [V]	Rs [Ω]	L1 [10^{-7} H]	R1 [Ω]	CPE1-T [10^{-3} F·s$^{CPE1-P-1}$]	CPE1-P ×10^{-1}	R2 [Ω]	CPE2-T [10^{-3} F·s$^{CPE2-P-1}$]	CPE2-P ×10^{-1}	f1 [Hz]	f2 [Hz]
0	7.33	4.34	12.78	2.59	9.02	56.08	7.16	3.69	6.98	1.89
-0.1	7.09	4.42	24.57	4.98	7.94	55.74	1.44	3.03	2.24	0.33
-0.2	7.23	4.32	8.03	9.20	3.42	56.04	8.02	6.58	319.59	0.54
-0.3	7.03	4.44	8.57	1.41	3.02	53.73	1.07	6.57	173.53	0.37
-0.4	7.36	4.19	6.78	5.30	4.06	52.69	9.36	6.16	570.60	0.50
-0.5	7.42	4.19	9.73	6.32	3.92	49.41	8.07	6.30	195.09	0.68
-0.6	7.56	4.17	9.85	4.41	4.34	50.54	4.9	6.60	220.66	1.30
-0.7	7.62	4.14	7.96	3.11	4.68	56.25	3.37	6.62	427.71	1.96
-0.8	7.73	4.08	8.18	3.30	4.55	58.18	2.55	6.83	448.44	2.6
-0.9	7.74	4.10	8.42	3.01	4.55	61.31	1.94	6.97	511.14	3.37

Where

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

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

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

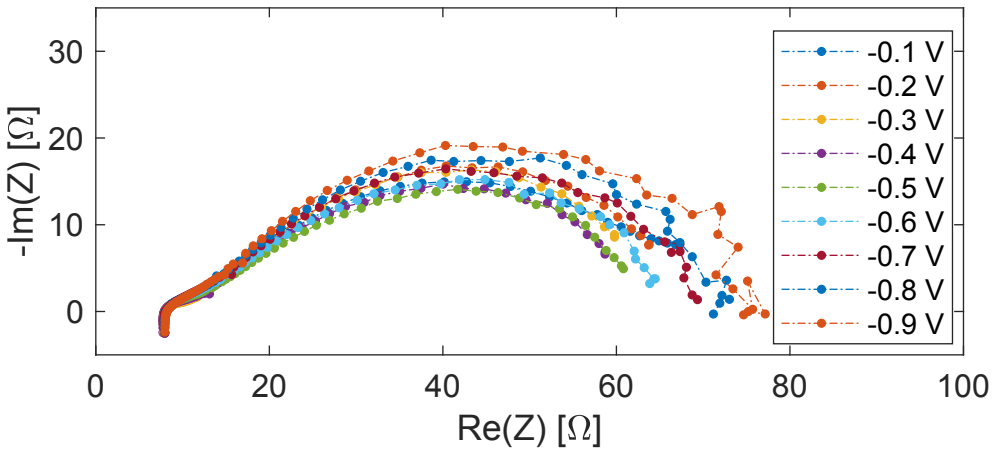

Fig. S 2 Nyquist plots at different bias voltages.

According to Eqns. 21 and 22

$$i(t) = \frac{\pi FD}{X^2}\sum_n (2n+1)\frac{(-1)^n\sqrt{k/D}\left(Ae^{\sqrt{k/D}X} - Be^{-\sqrt{k/D}X}\right) + \left(n+{}^1\!/_2\right)\pi/_X(A+B)}{\left({}^k\!/_D + \left(\left(n+{}^1\!/_2\right)\pi/_X\right)^2\right)e^{\left(((n+1/2)\pi/X)^2 D + k\right)t}}$$

$$i(t) = \frac{\pi FD}{X^2}\sum_n (2n+1)\frac{(-1)^n\sqrt{k/D}\left(Ae^{\sqrt{k/D}X} - Be^{-\sqrt{k/D}X}\right) + \left(n+{}^1\!/_2\right)\pi/_X(A+B)}{\left({}^k\!/_D + \left(\left(n+{}^1\!/_2\right)\pi/_X\right)^2\right)e^{\left(((n+1/2)\pi/X)^2 D + k\right)t}} + A_C e^{-\frac{1}{RC}t}$$

i(t) is the sum of several exponential formulas, which are derived from the diffusion of H atoms in the metal bulk, decomposition of adsorbed species on the catalyst surface, and the discharge of the capacitor by electrical double layer. Since the term for the diffusion of H atoms is the infinite sum of exponential formulas, in order to solve the numerical solutions, the term of the H atom diffusion is approximated by the sum of n = 0 and n = 1. Because the terms for H atom diffusion and the capacitor discharge decay very quickly, *i*(t) mainly consists of the term for the decomposition of the intermediates when *t* is sufficiently large. In this work, the raw data were fitted with $FA_H e^{-k_1 t}$ or $F\left(k_1 B_H e^{-k_1 t} + \frac{k_1 k_2}{k_1 + k_2} B_H e^{-k_2 t}\right)$ from 50 s to 100 s as shown in Figs. S 3 and S 4. The sum of the terms for the H atom diffusion and the capacitor discharge was fitted well with the residual.

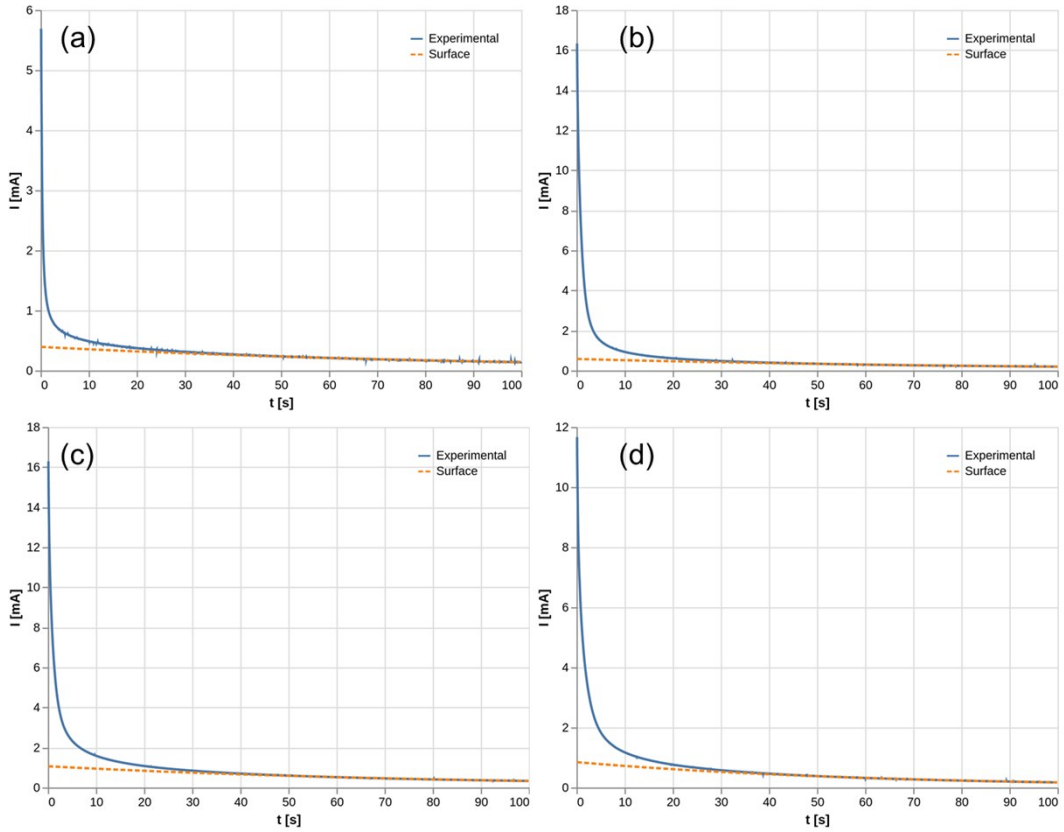

Fig. S 3 Fitting results of the decomposition part under dry Ar gas atmosphere at cathode side. (a) -0.2 V (b) -0.5 V (c) -1.5 V (d) -1.9 V.

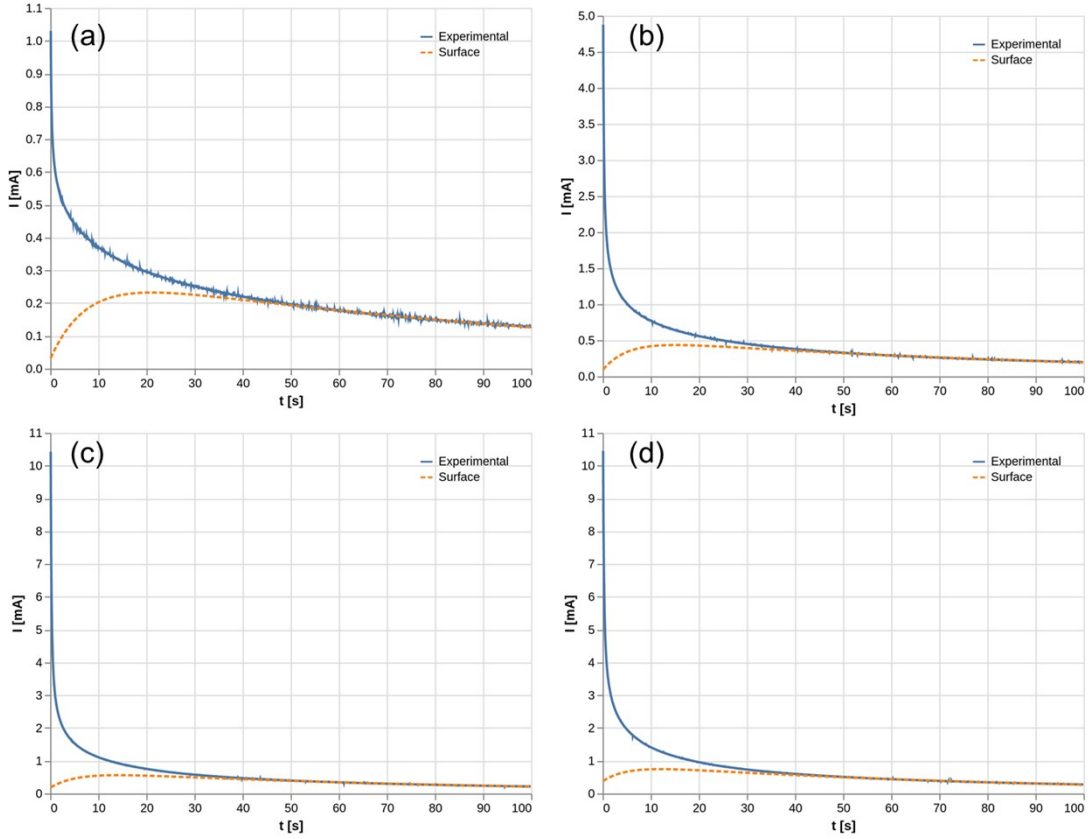

Fig. S 4 Fitting results of the decomposition part under dry N_2 gas atmosphere at cathode side. (a) -0.2 V (b) -0.5 V (c) -1.5 V (d) -1.9 V.

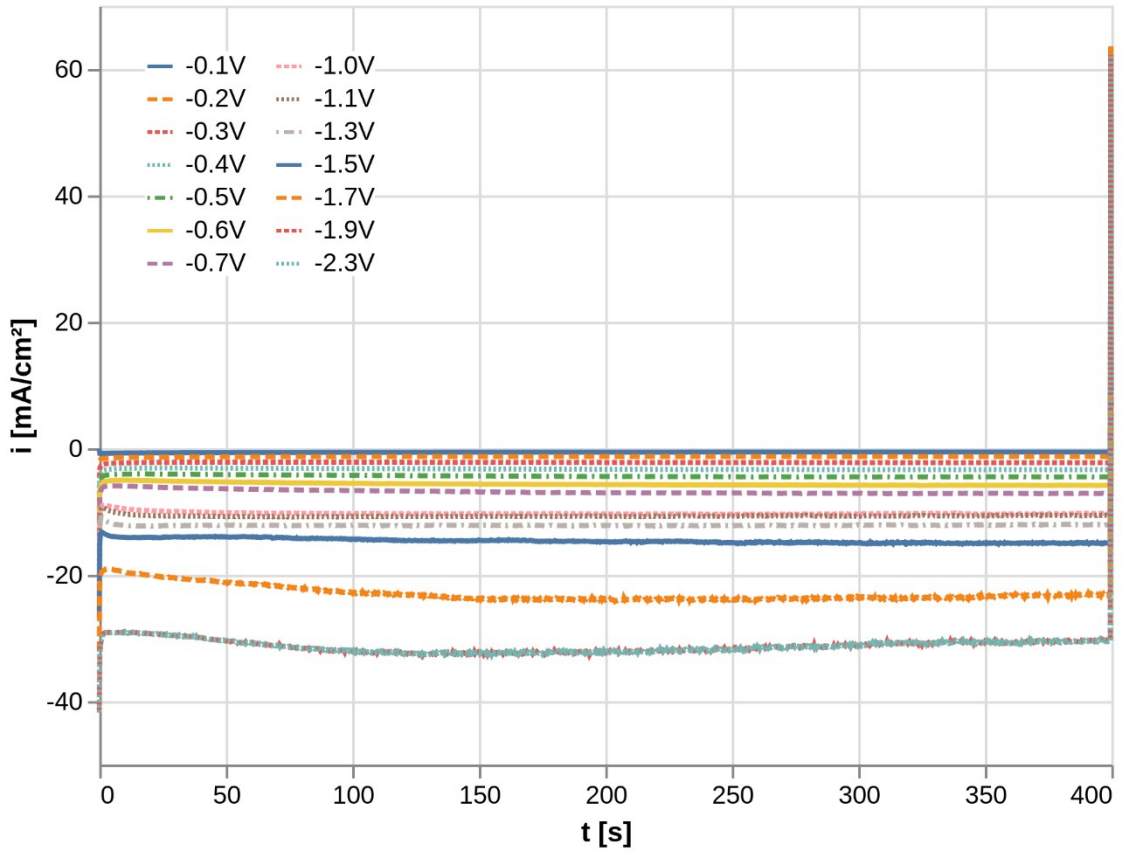

Fig. S 5 Current density at different applied voltages. Cathode was supplied with dry N_2.

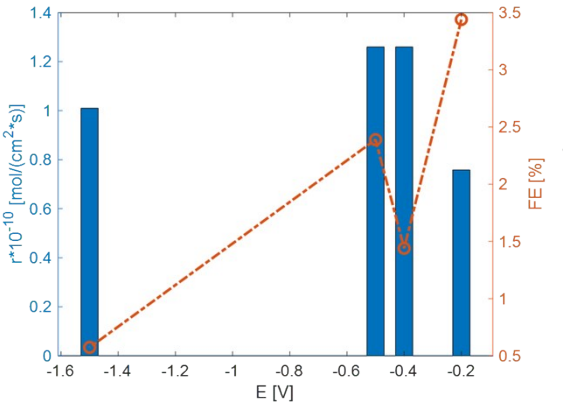

Fig. S 6 Electrolysis results of a cell with RuO_2 cathode catalyst (0.075 g) under dry N_2 cathode and 3% humidified H_2 anode atmosphere: Production rate and corresponding Faradic efficiency (FE) of NH_3

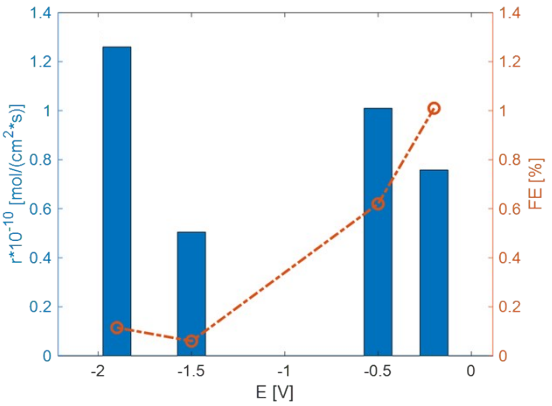

Fig. S 7 Electrolysis results of a cell with 0.075 g Fe/BZY cathode catalyst under dry N_2 cathode and 3% humidified H_2 anode atmosphere: Production rate and corresponding Faradic efficiency (FE) of NH_3.

Table S 4 Fitting results with RuO_2 cathode catalyst under dry Ar gas atmosphere at cathode side.

E [V]	k_1 [10^{-2} s^{-1}]	β_H [10^{-7} mol]	1/(RC) [s^{-1}]
-0.5	1.3	2.7	2.1
-1.5	1.3	3.5	4.7
-1.9	1.6	4.8	5.2

Table S 5 Fitting results with RuO_2 cathode catalyst under dry N_2 gas atmosphere at cathode side.

E [V]	k_1 [10^{-2} s^{-1}]	k_2 [10^{-2} s^{-1}]	β_H [10^{-8} mol]	$\beta_{NH\ or\ N_2H}$ [10^{-8} mol]	1/(RC) [s^{-1}]
-0.5	2.9	3.3	1.9	2.8	10.7
-1.5	2.9	3.3	7.1	2.6	9.7
-1.9	1.6	2.4	20	9.4	3.1

Table S 6 Fitting results with Fe/BZY cathode catalyst under dry Ar gas atmosphere at cathode side.

E [V]	k_1 [10^{-2} s^{-1}]	β_H [10^{-7} mol]	1/(RC) [s^{-1}]
-0.5	1.1	1.7	3.3
-1.5	1.0	2.7	4.1
-1.9	1.1	2.5	4.5

Table S 7 Fitting results with Fe/BZY cathode catalyst under dry N_2 gas atmosphere at cathode side.

E [V]	k_1 [10^{-2} s^{-1}]	k_2 [10^{-2} s^{-1}]	β_H [10^{-8} mol]	$\beta_{NH\ or\ N_2H}$ [10^{-8} mol]	1/(RC) [s^{-1}]
-0.5	1.7	1.9	9.7	3.2	3.6
-1.5	1.3	1.8	20	10	4.4
-1.9	1.4	1.8	17	6.8	4.6