

Improvements in the Evaluation of Electrocatalytic Ammonia Oxidation Reactions

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1. Experimental

1.1 Chemicals

Nickel foam (NF, 0.5 mm thickness, Canrd), HCl (Guangfu, 37%), NH₄F (Aladdin, 98.0%), CO(NH₂)₂ (Aladdin, > 99.5%), Co(NO₃)₂·6H₂O (Aladdin, 99.0%), NH₄Cl (Macklin, ≥ 99.5%); ¹⁵NH₄Cl (Aladdin, ≥ 98.0%), Acetonitrile (Adamas, Water ≤ 50 ppm, 99.9%), Tetra-n-butylammonium hexafluorophosphate (Adamas, 99%+).

1.2 Synthesis of cobalt nitride/NF

1.2.1 Preparation of Co(OH)₂/NF

The nickel foam (NF) was cut into dimensions of 3 cm (W) × 5 cm (L), followed by treating in 3 M HCl solution with the assistance of ultrasonic for 15 min to remove the surface oxide layer. Then, repeated washing with deionized water and ethanol until the pH=7. After that, the NF was dried in a vacuum oven at 60 °C for 12 h.

In a typical procedure, NH₄F (2 mmol), CO(NH₂)₂ (5 mmol) and Co(NO₃)₂·6H₂O (2 mmol) were dissolved in 50 mL deionized water with vigorous stirring for 30 min. Then the resulting solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave. Then, one piece of cleaned NF was immersed into the solution with the angle of 60°. The autoclave was sealed and heated at 120 °C for 12 h, and then allowed to cool down to room temperature. The obtained material was washed for three times with deionized water to remove the surface solution and sediment. The Co(OH)₂ nanowires on NF (called as Co(OH)₂/NF) was obtained after the treatment in a vacuum oven at 60 °C for 12 h.

1.2.2 Preparation of cobalt nitride/NF

The Co(OH)₂/NF was placed into a tube furnace system and treated in pure ammonia atmosphere with the flow rate of 30 mL min⁻¹, followed by heating at 400 °C for 2 h.

1.3 Material characterizations

X-ray powder diffraction (XRD) patterns were obtained on a Bruker D8 advance powder diffractometer, using Cu Kα (λ = 1.5418 Å) as the radiation source. The scanning electron

microscopy (SEM) images were taken on a Hitachi Regulus 8230.

1.4 Electrochemical measurements in aqueous electrolyte

Electrochemical measurements were conducted in a three-electrode cell on a CHI660e workstation using a graphite rod as counter electrode, a Hg/HgO as the reference electrode and the as-prepared cobalt nitride material (dimensions 10 × 20 mm, thickness 0.5 mm) as the working electrode. In order to remove air, the electrolyte (1 M KOH + 0.5 M NH₃) was bubbled with Ar gas flow for 20 min before test. CV tests were performed at a scan rate of 10 mV s⁻¹.

1.5 Electrochemical measurements in non-aqueous electrolyte

Bio-Logic VMP2 was used for the following electrochemical experiments. The two-electrode electrolysis of NH₃ was performed using two identical platinum wire (Φ 0.5 mm, length 37 mm) as the anode and cathode. The three-electrode voltammetry in acetonitrile with 0.1 M tetra-n-butylammonium hexafluorophosphate was performed with a Pt wire as working electrode, a Pt mesh (dimensions 10 × 10 mm, thickness 0.5 mm) as counter electrode, and a Ag^{0/+} (0.01 M AgNO₃ in acetonitrile) reference electrode. All electrochemical measurements were reported vs NHE, using ferrocene/ferrocenium (Fc^{0/+}) as a calibrating redox couple.^{1, 2} All cyclic voltammograms (CVs) were conducted at a scan rate of 20 mV s⁻¹ in a single-compartment cell. NH₃ gas (HuChen, 99.9999%) was bubbled for 2-3 min until the solution was saturated.

1.6 In situ DEMS analysis

Differential electrochemical mass spectrometry (DEMS, Linglu Shanghai) measurements were carried out for in situ analysis of gas products generated on the working electrode, such as N₂ (m/z: 28), ¹⁵N₂ (m/z: 30). The working electrode was as-prepared cobalt nitride/NF. The PTFE membrane (50 μm thickness, 20 nm pore) that only allows the penetration of volatile and hydrophobic species was used in the measurements.

1.7 On line MS

Gas products generated from both the working and counter electrodes were analyzed using a Hiden Analytical Mass Spectrometer (QIC-20), which equipped with capillary, quadrupole

mass analyser and Faraday/secondary electron multiplier detectors. MID mode was applied to monitor various possible gases, such as H₂ (m/z: 2), N₂ (m/z: 28), O₂ (m/z: 32), NO (m/z: 30), NO₂ (m/z: 46) and N₂O (m/z: 44). On line MS is used to detect the gas products that have separated from the electrolyte.

2. Calculation of electrode potentials

The aqueous potentials were confirmed using available thermochemical data from the CRC Handbook³ and NIST.⁴ The solvation energies of NH₃ in aqueous and acetonitrile was taken from the work reported by Miller.⁵

Table S1 Thermodynamic Data for Hydrogen-and Nitrogen-Containing Species

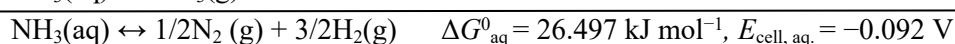
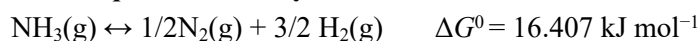
	ΔH_f^0 (298.15 K) kJ mol ⁻¹	S^0 (298.15 K) J K ⁻¹ mol ⁻¹
H ₂ (g)	0	130.68 ± 0.003
N ₂ (g)	0	191.609 ± 0.004
NH ₃ (g)	-45.94 ± 0.003	192.77 ± 0.35
NH ₄ ⁺ (aq.)	-133.26 ± 0.25	111.17 ± 0.40
H ₂ O(l)	-285.830 ± 0.4	69.95 ± 0.03
OH ⁻ (aq.)	-230.015 ± 0.4	-10.90 ± 0.2
H ⁺ (aq.)	0	0

2.1 For NH₃(g) / N₂ (g):

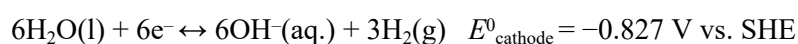


$$\Delta H^0 = 45.94 \text{ kJ mol}^{-1}, \Delta S^0 = 99.0545 \text{ J mol}^{-1}\text{K}^{-1}, \Delta G^0_1 = 16.407 \text{ kJ mol}^{-1}$$

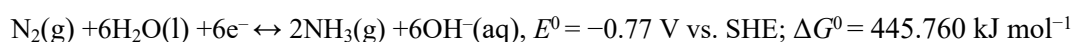
2.2 In aqueous electrolyte:



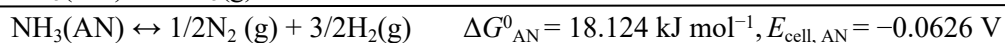
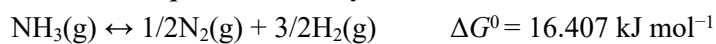
Cathode:



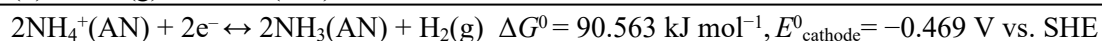
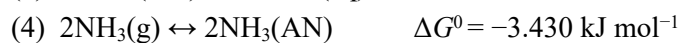
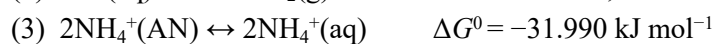
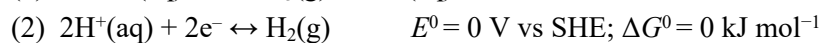
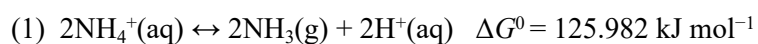
Anode:



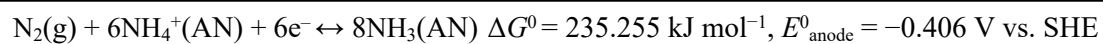
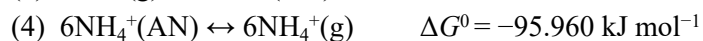
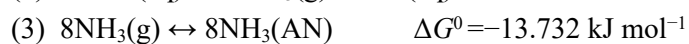
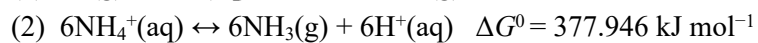
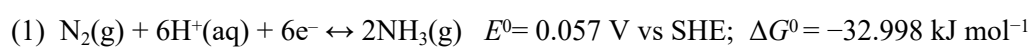
2.3 In non-aqueous electrolyte:



Cathode:



Anode:



3. Figures

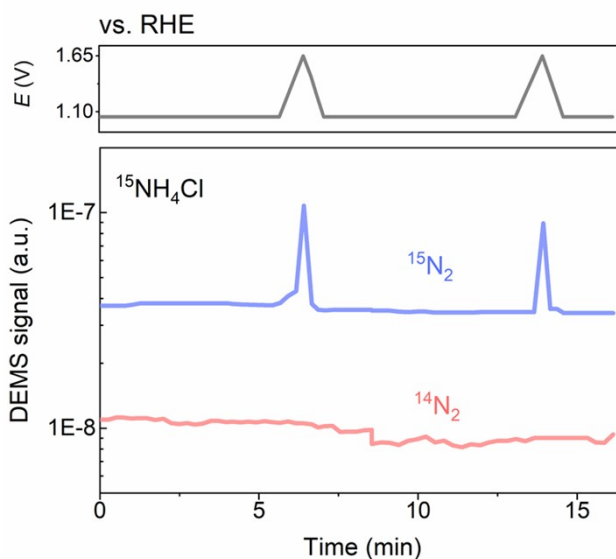


Fig. S1 DEMS signals of $^{14}\text{N}_2$ and $^{15}\text{N}_2$ in the isotope EAOR measurements for the home-made $\text{Ni}(\text{OH})_2$ nanosheets with local tensile strain (tst- $\text{Ni}(\text{OH})_2$ catalyst) as reported in our previous work.⁶ During the CV test, only $^{15}\text{N}_2$ was observed, confirming all nitrogen of the N_2 gas product is derived from ammonia. Electrochemical measurements were conducted in a three-electrode cell using tst- $\text{Ni}(\text{OH})_2$, Pt wire, and Ag/AgCl (saturated KCl solution) as the working, counter, and reference electrode, respectively. The electrolyte was 1.5 M NaOH + 0.5 M $^{15}\text{NH}_4\text{Cl}$ aqueous solution. The scan rate is 10 mV s^{-1} .

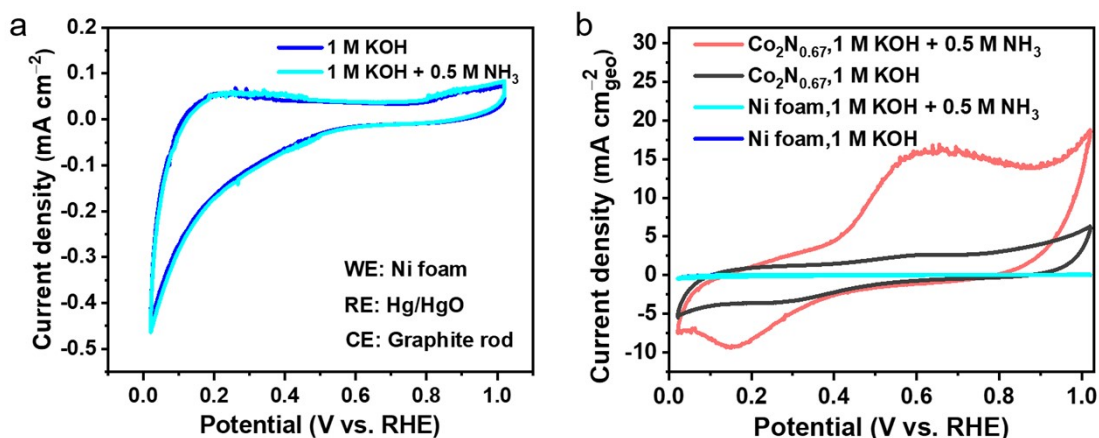


Fig. S2 CV curves of the Ni foam in the aqueous electrolytes of 1 M KOH and 1 M KOH + 0.5 M NH_3 . The scan rate is 10 mV s^{-1} .

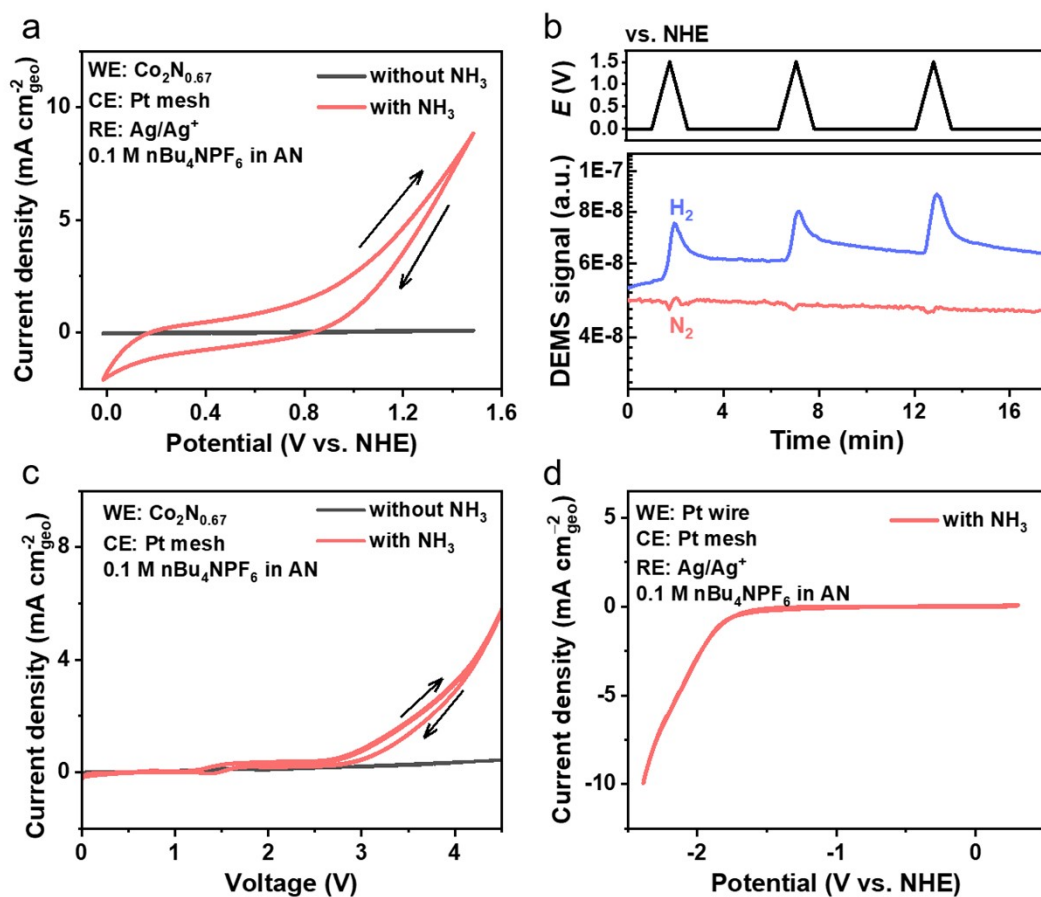


Fig. S3 EAOR measurements of as-prepared $\text{Co}_2\text{N}_{0.67}$ in nonaqueous electrolytes. **a.** CV curves of $\text{Co}_2\text{N}_{0.67}$ in the nonaqueous electrolytes of 0.1 M nBu_4NPF_6 in acetonitrile with/without ammonia. **b.** On line MS analysis of gas products during the EAOR test. **c.** CV curves of ammonia electrolysis in a two-electrode cell. **d.** HER of the Pt electrode in the nonaqueous electrolyte. The scan rate is 20 mV s^{-1} . The potential is converted according to $E_{\text{NHE}} = E_{\text{Ag}0/+} + \Delta E_{(\text{Ag}0/+ - \text{Fc}0/+)} + 0.400 \text{ V} = E_{\text{Ag}0/+} + 0.489 \text{ V}$.

References

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