

Supporting Information

Real-time screening of Ni_xB_y bifunctional electrocatalyst for overall NH₃ synthesis via SG-TC SECM

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Chemicals and reagents used

Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Loba Chemie while sodium borohydride (NaBH_4 , anhydrous) was purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 37%) and sulfuric acid (H_2SO_4) were bought from Merck. On the other hand, ammonium chloride (NH_4Cl , 99%), salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$, 99.5%), sodium nitroprusside ($\text{C}_5\text{FeN}_6\text{Na}_2\text{O}$, 99%), trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) were bought from Loba Chemie. Reagents such as sodium sulphate (Na_2SO_4 , 99%) and potassium hydroxide (KOH, 85%), sodium hydroxide (NaOH, 98%), sodium hypochlorite solution (NaClO , 4-6%) and hydrogen peroxide solution (H_2O_2 , 5%) were also purchased from Loba Chemie. High purity $^{14}\text{N}_2$ (99.999%), $^{15}\text{N}_2$ (99%) and Ar gas (99.999%) cylinders were purchased from Sigma. All the chemicals and reagents used were of analytical grade and used as such without purification. All solutions were prepared using deionized water obtained from Millipore system (>15 M Ω).

Electrochemical investigations

A home made two compartment H-cell was used to perform the half-cell and full-cell studies under room temperature conditions only. The cell was separated by a Nafion N117 membrane which was cleansed prior fitting by boiling in deionized water (>14 M Ω) for 0.5 h and subsequently in H_2O_2 (5%) solution at 80 °C for 0.5 h followed by boiling in 0.05 M H_2SO_4 for 1 h. A glassy carbon electrode (GC \varnothing 2 mm) was used as working electrode (WE), Hg/HgO/1M NaOH electrode was used as reference electrode (RE) and Pt mesh was used as a counter electrode (CE) respectively. Polishing of WE was carried out using different grades of alumina slurry (0.3 to 0.05 μm , PINE instrument, USA) on Nylon polishing cloth

(SM 407052, AKPOLISH) till mirror finishing was obtained and then was ultrasonicated in deionized water for removal of alumina particles (if any). Catalyst powder was finely grinded in mortar pestle for 30 min. while the catalyst slurry was prepared by dissolving 1.25 mg of catalyst powder in the mixture of isopropyl alcohol (20 μL) and deionized water (480 μL). The above slurry was kept under bath sonication till the homogeneous dispersion was observed. The ink was then drop-casted on WE and dried at room temperature in open atmosphere. Electrochemical measurements comprising linear sweep voltammetry (LSV), chronoamperometry (CA), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed using Biologic VSP 300 Potentiostat in 0.1 M KOH electrolyte (pH=13). All the potentials were reported w.r.t reversible hydrogen electrode (RHE) by conversion formula:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E^{\circ}_{\text{Ag/AgCl}} + 0.059 \text{ pH}$$

Charge transfer resistance was calculated using EIS where in a DC potential of -0.2 V vs. RHE was applied over an AC perturbation of 10 mV amid a frequency of 10 Hz to 200 KHz in a logarithmic frequency step over a single sine wave. A semicircular behavior was observed in corresponding Nyquist plot which gave the values for solution resistance (R_s), polarization resistance (R_p) and charge transfer resistance (R_{ct}) respectively. The double layer capacitance of electrocatalysts and electrochemical surface area (ECSA) was calculated by performing cyclic voltammetry at different scan rates (10 mV s^{-1} to 320 mV s^{-1}) under the non-faradaic region between a potential window of 0.28 to 0.38 V vs. RHE in N_2 -saturated 0.1 M KOH solution. The average mean current densities were plotted against scan rates, and the slope of linear curve delivered the double-layer pseudo-capacitance (C_{dl}). ECSA was further calculated by dividing C_{dl} by specific capacitance of flat planar

electrode surface *i.e.* taken as $40 \mu\text{Fcm}^{-2}$ in this case.

Physical characterization

The P-XRD patterns for Ni_xB_y catalysts were reconnoitered using PANalytical X'PERT pro diffractometer in the 2θ range of $5-80^\circ$ with Cu-K α radiation ($\lambda=0.1542 \text{ nm}$, 40 kV, 40 mA) at a scan speed of 2° per minute. The morphological analysis was done using field emission-scanning electron microscopy (FE-SEM, Hitachi, Japan, SU8010) and transmission electron microscopy (HR-TEM, JEOL, Jem 2100 plus). The high resolution TEM (HR-TEM) images were recorded at 200 kV. The XPS measurements were performed using the Thermo scientific NEXSA surface analysis with a micro-focused ($400 \mu\text{m}$, 72 W, 12000 V) monochromatic Al K α (1486.6 eV) hemispherical analyzer and 128 channel plate detectors under ultrahigh vacuum (UHV 8-10 mbar). All the spectrum were calibrated with reference to C 1s spectra. The ^1H NMR spectra was utilized to determine and quantify the $^{14}\text{NH}_4^+$ and $^{15}\text{NH}_4^+$ produced in electrolyte samples after NRR isotope labelling experiments and in standard samples using JEOL JNM-ECS 400 Hz spectrometer at ambient probe temperatures. MP-AES analysis was carried out using Agilent 4200 Microwave Plasma Atomic Emission Spectrometer with conc. HNO_3 as standard reference solution for calibration.

Quantification of Ammonia

Indophenol blue method: The final product (*i.e.* NH_3) obtained after electrolysis was quantified using indophenol blue method with the help of UV-Vis spectroscopy. Firstly, 2 mL of electrolyte sample (after 2 h of chronoamperometry) was collected from the cathodic compartment of H-cell in which 2 mL of solution containing mixture of 5% salicylic acid and 5% trisodium citrate in

1 M KOH is added immediately. Consequently, 1 mL of 0.05 M NaClO and 200 μ L of 1% sodium nitroprusside as a colouring agent was added to the same electrolyte sample. The solution is incubated for 2 h to develop stable colour, and absorbance is measured at a wavelength of 655 nm.¹ The UV-vis spectrum is obtained for different concentrations of NH₃ (0.2, 0.4, 0.8, and 1 ppm) using standard NH₄Cl solution to draw a calibration curve exhibiting a linear relationship between absorbance and concentration value from the fitting curve ($y = 0.285x + 0.109$, $R^2 = 0.99663$).

¹H-NMR spectroscopy: After NRR, 25 ml of the electrolyte was taken out and mixed with 1M HCl and then concentrated to 1 mL, from which 0.6 ml of the resulting liquid was taken and 0.4 ml of DMSO-d₆ is added as an internal standard. The produced ammonia was confirmed by using proton-nuclear magnetic resonance spectroscopy measurements (¹H NMR)² with water gate suppression sequence and a relaxation delay of 3 s, 8000 scans using a pulse sequence by pulse field gradient (PFG) unit.

Quantification of oxygen (O₂) by eudiometry and gas chromatography: Evolution of O₂ at applied potentials was detected quantitatively by means of a gas chromatograph (GC, SHIMADZU, GC-2030). A SHIMADZU Rt-Q-BOND column is installed in GC having two detectors, namely, a thermal conductivity detector (TCD) and a flame ionization detector (FID) to measure H₂/O₂. The carrier gas used was N₂.³ The produced O₂ was collected from the outlet of anode compartment and the sample was run in GC for O₂ quantification method in the software from which the chromatogram was obtained showing retention time of 1.2 for O₂. The area under the curve was utilized to quantify oxygen from GC. On the other hand, in eudiometry method, a burette was fitted into the H-cell with electrode at the bottom where the OER can take place.

The O₂ bubbles generated during the reaction go upwards and get collected at the top of the burette creating an air gap. The readings were taken for different time intervals and after 2 h of overall ammonia synthesis, the O₂ yield rate was calculated from the final reading.

Gas cleansing procedures

The commercial gas-supplies were cleansed before performing any set of NRR experiment by passing them through a scrubbing solution consisting of alkaline KMnO₄ and dilute H₂SO₄ solution which will remove any trace NH₄⁺ and NO_x (NO, NO₂, N₂O) impurities. To assure that the gases have been cleansed or not, the impurities before and after passing through the scrubbing solution were quantified using colorimetric method and gas chromatography-mass spectroscopy (GC-MS) method.

The NO_x (NO/NO₂) was trapped in alkaline KMnO₄ solution technique while NH₄⁺ impurities were trapped in acidic solution and both were quantified using UV-Vis. spectrophotometry before and after purification. On the other hand, the N₂O impurities were detected and quantified by means of GC-MS in SIM (selected ion monitoring) mode at m/z value of 44 for N₂O.

NO₂⁻ quantification by spectrophotometry method:

Quantification of nitrite was performed via diazotization reaction by using sulphanilamide under acidic environment followed by coupling with N-(1-Naphthyl) ethylenediamine dihydrochloride which result into formation of pink colored azo dyes with corresponding peak at 540 nm respectively. Initially, standard solutions are prepared using NaNO₂ stock solution with different concentrations *i.e.* 2 to 60 µg L⁻¹. Afterwards, two reagents are prepared separately, 0.5 g of sulphanilamide in 50 mL of 2 M HCl *i.e.* **A** and 20 mg of N-(1-Naphthyl) ethylenediamine

dihydrochloride in 20 mL of deionized H₂O *i.e.* **B**. Briefly, 5 mL of standard or sample solution are taken in glass vials followed by addition of 0.1 mL of A which is then allowed to stand for 10 min. Afterwards, 0.1 mL of B is added to above solution respectively.⁴ The solution mixture was kept undisturbed for 30 min and amount of NO₂⁻ is estimated under wavelength range of 440-600 nm, from which calibration curves were extracted. The samples after and before purification were analysed using the same procedure.

N₂O quantification by gas chromatography-mass spectroscopy (GC-MS): The trace N₂O is detected and quantified with the help of GC-MS in SIM (selected ion monitoring) mode by selecting the m/z value of 44 corresponding to N₂O. The parameters to acquire the data can be set with the column oven temperature of 40 °C and an injection temperature of 150 °C. The column flow is kept at 0.99 mL min⁻¹ with an ion source temperature and interface temperature of 200 °C and 220 °C respectively. The obtained chromatograms are used to draw a calibration curve and calculate the amount of N₂O present in feeding gas-supplies.⁵

The quantified amounts of NO_x/NH₄⁺ impurities before and after purification by scrubbing solution by colorimetric and GC-MS method are detailed as follows:

Ar (99.99%, Sigma)

Before purification:

NO/NO₂: 0.6 ppm; **N₂O:** <0.01 ppm; **NH₄⁺:** not detected

After purification:

NO/NO₂: not detected; **N₂O:** not detected; **NH₄⁺:** not detected

¹⁴N₂ (99.99% Sigma)

Before purification:

NO/NO₂: 1.1 ppm; **N₂O:** 0.06 ppm; **NH₄⁺:** 0.09 ppm

After purification:

NO/NO₂: <0.01 ppm; **N₂O:** <0.01 ppm; **NH₄⁺:** not detected

¹⁵N₂ (99.99% Sigma)

Before purification:

NO/NO₂: 1.2 ppm; **N₂O:** 0.07 ppm; **NH₄⁺:** 0.08 ppm

After purification:

NO/NO₂: <0.01 ppm; **N₂O:** <0.01 ppm; **NH₄⁺:** not detected

Isotope labelling experiments

The NRR isotope labelling experiment were performed by using ¹⁵N₂ (Sigma-Aldrich 99 atom% ¹⁵N) as the feeding gas. The ¹⁵N₂ gas was purified to eliminate the reducible/labile N-containing impurities.⁶ A total of 250 mL gas was purged into the cathode compartment of cell before the electrolysis to carry out NRR under static conditions at -0.2 V for 2 h. The electrolyte sample was prepared for NMR analysis and assessed using the same.⁶

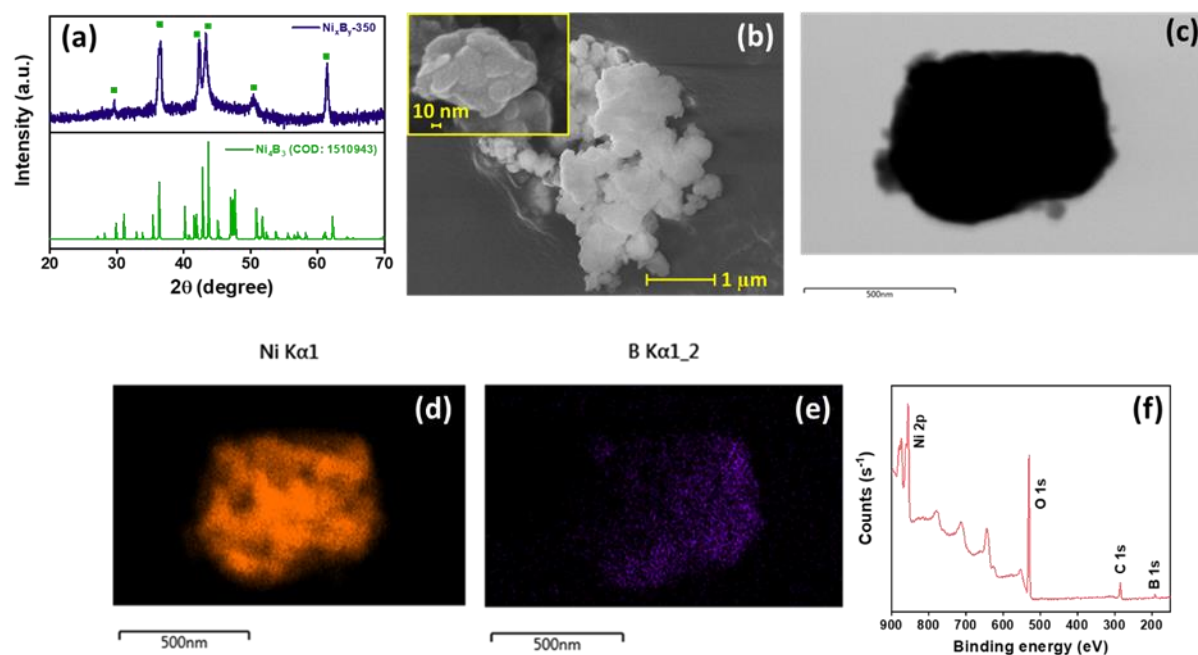


Fig. S1A (a) P-XRD pattern of annealed Ni_xB_y (SR) catalyst at 350 °C, (b) FE-SEM image of Ni_xB_y (CR), (c-e) TEM-EDS mapping of Ni_xB_y (SR) catalyst showing uniform distribution of Ni and B over scanned area and (f) XPS survey spectrum of Ni_xB_y (SR) catalyst.

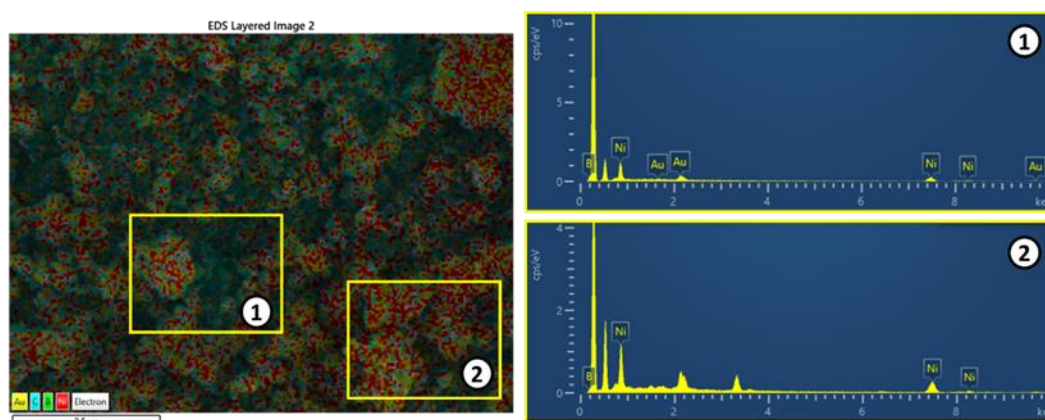


Fig. S1B EDS-dot mapping image showing scanning over two different selection areas in Ni_xB_y (SR) catalyst and EDS spectrum extracted from the same.

Table S1. MP-AES elemental composition of Ni_xB_y (SR) catalyst.

Element	Weight%	σ (Standard deviation)
Ni K	73.6	0.7
B K	11.8	0.9

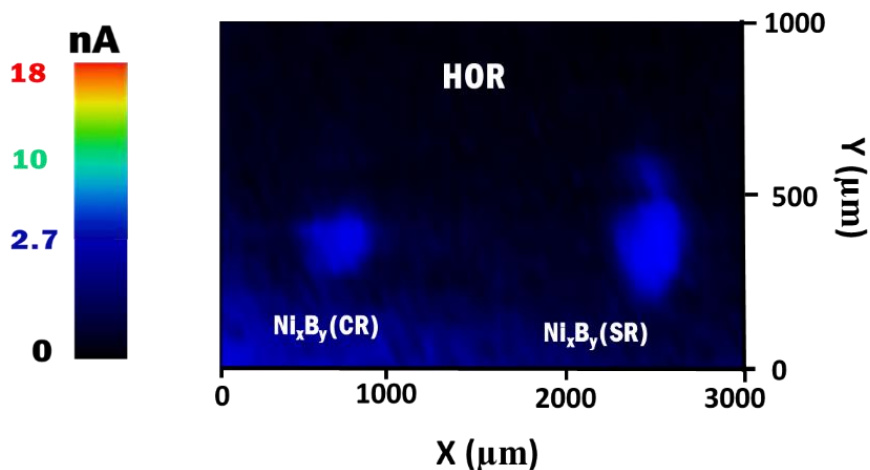


Fig. S2A 2D-SECM images of Ni₄B₃ catalysts in Ar-saturated 0.1 M KOH depicting tip current response for HOR respectively over Pt-UME via SG-TC mode.

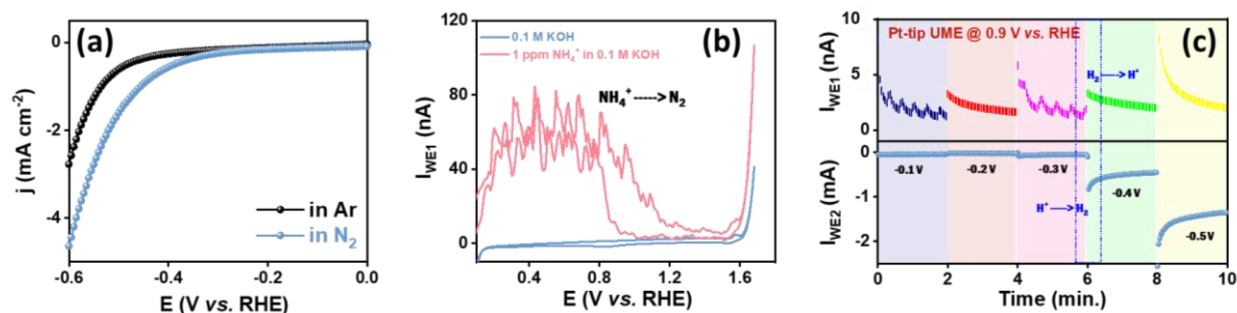


Fig. S2B (a) LSV curves for Ni_xB_y (CR) in Ar- and N₂-saturated 0.1 M KOH, (b) CV recorded over Pt-UME in absence and presence of NH₄⁺ in electrolyte to witness ammonia oxidation and (c) SG-TC SECM mode employed to perform sequential CA where HER takes place at WE2 while HOR takes place over WE1 on Ni_xB_y (SR) catalyst.

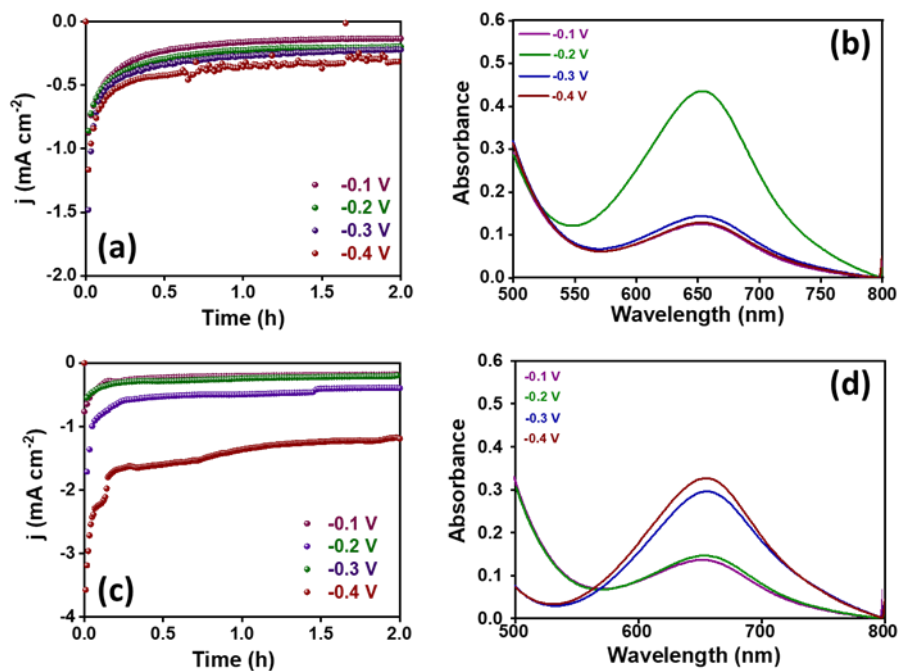


Fig. S3 (a) and (c) CA curves acquired by Ni_xB_y (CR) and Ni_xB_y (SR) respectively after NRR at different potentials between -0.1 and -0.4 V vs. RHE, (b) and (d) respective UV-Vis absorbance curves obtained after quantification by Indophenol blue method.

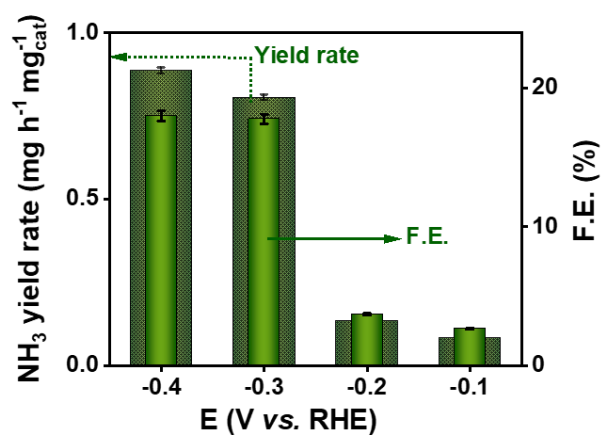


Fig. S4A Bar graph representing the F.E. and NH₃ yield rates after NRR by Ni_xB_y (CR) catalyst after 2 h of electrolysis at different potentials.

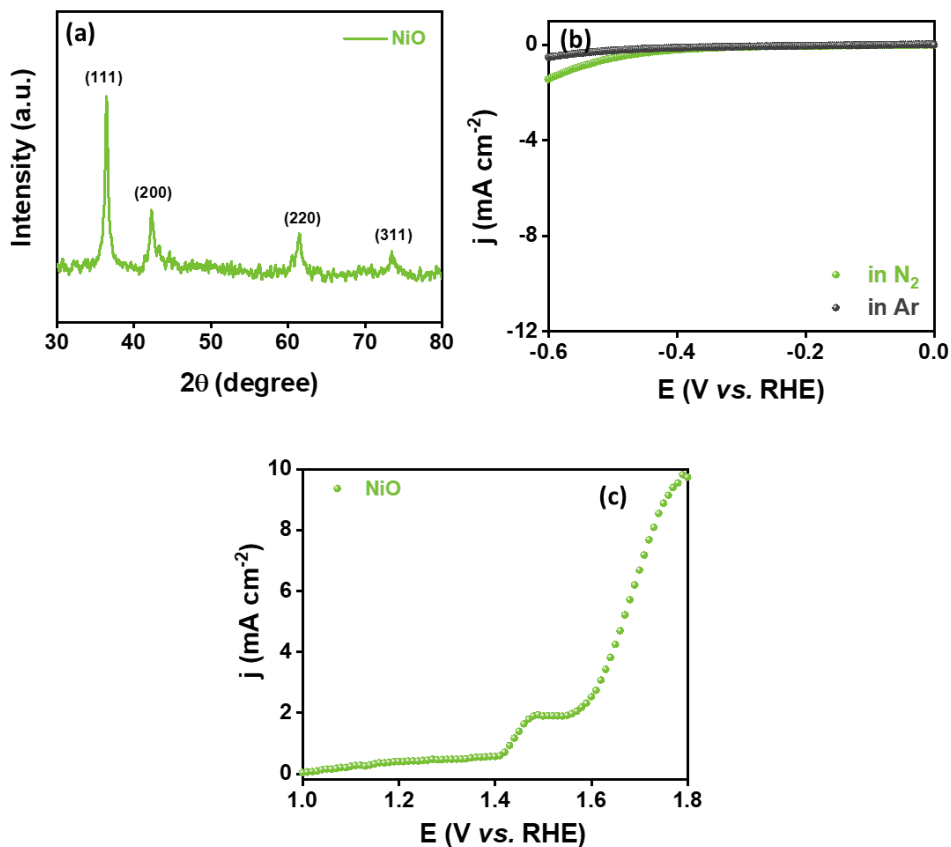


Fig. S4B (a) P-XRD pattern for as-synthesized NiO control catalyst, (b) LSV curves depicting the NRR and (c) OER performance of NiO catalyst in 0.1 M KOH respectively.

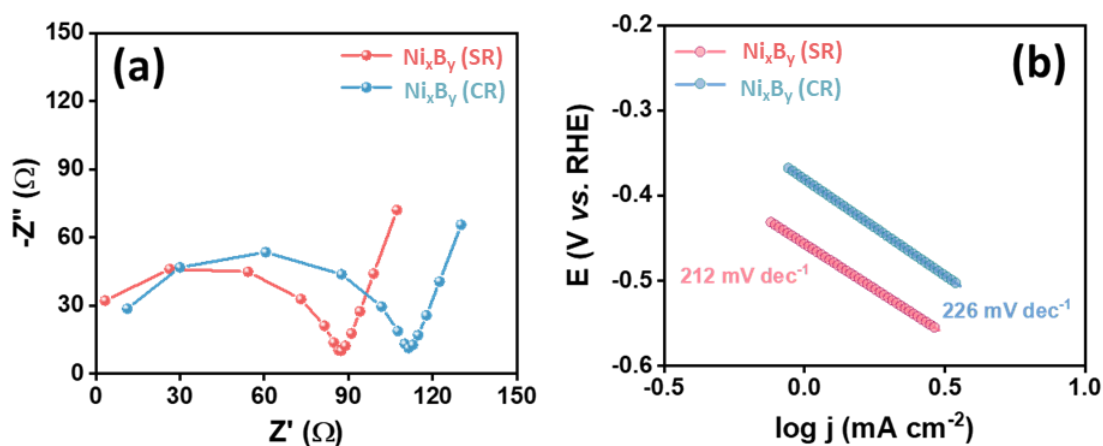


Fig. S5 (a) Nyquist plots and (b) Tafel plots for Ni_xB_y catalysts in 0.1 M KOH.

Table S2. Calculations from EIS and ECSA analysis for both catalysts.

Electrocatalyst	EIS analysis			ECSA analysis	
	R_s	R_p	R_{ct}	C_{dl}	ECSA
Ni_xB_y (SR)	2.12 Ω	85.63 Ω	83.5 Ω	2.6 mF	6.5 cm^2
Ni_xB_y (CR)	10.8 Ω	111.8 Ω	101 Ω	2.18 mF	5.4 cm^2

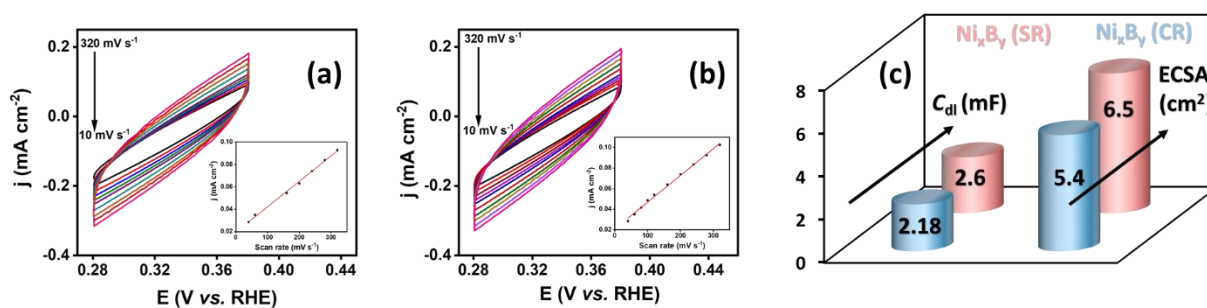


Fig. S6 (a) and (b) CV acquired in non-faradic region at different scan rates for Ni_xB_y (CR) and Ni_xB_y (SR) respectively and inset shows the scan rate vs. current density linear plots. (c) Bar graph comparison of ECSA and C_{dl} values of both catalysts.

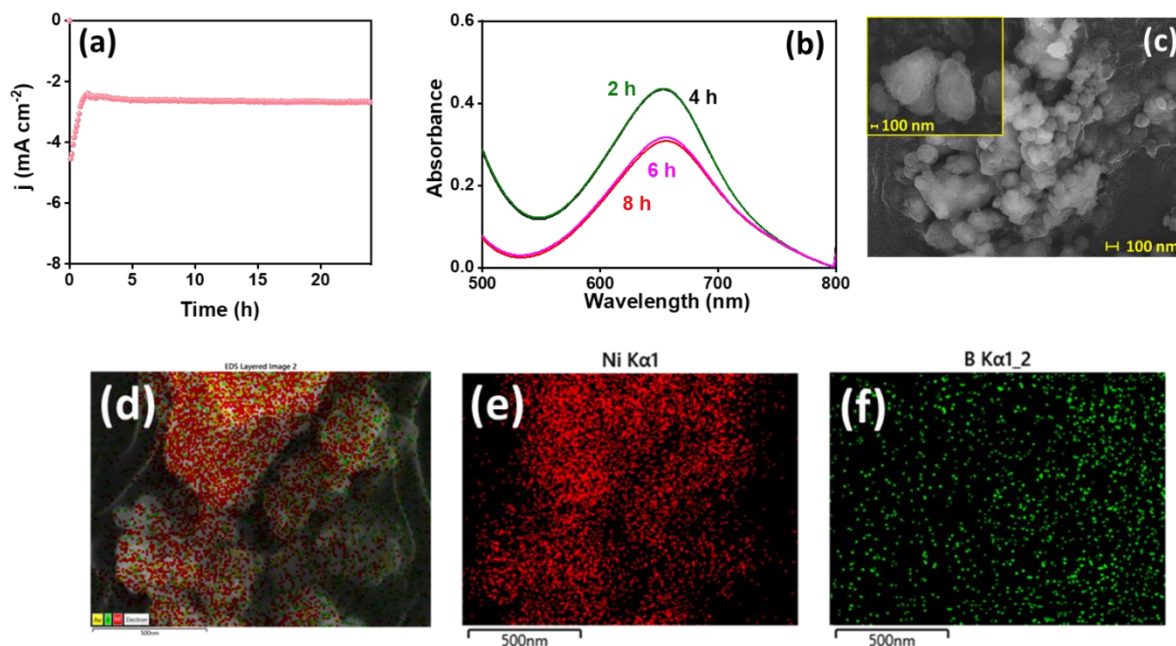


Fig. S7A (a) NRR stability tests for 24 h over Ni_xB_y (SR) catalyst in 0.1 M KOH, (b) UV-Vis. absorbance curve acquired after stability tests, (c) FE-SEM image and (d-f) EDS dot mapping images of Ni_xB_y (SR) after prolonged NRR durability measurements.

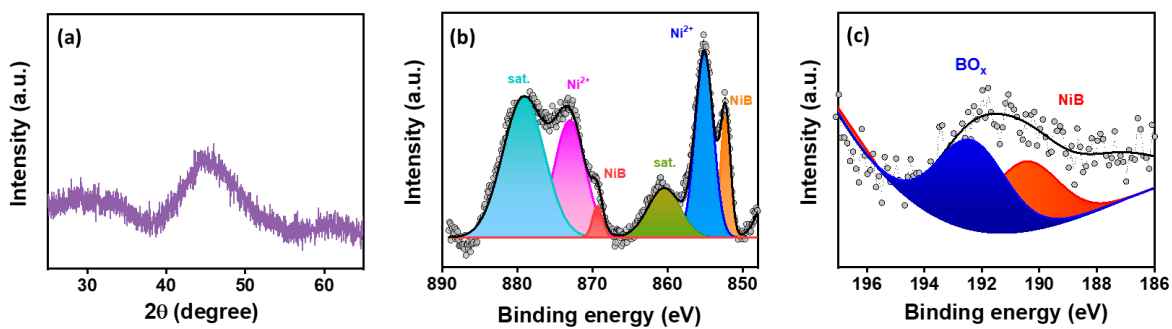


Fig. S7B (a) P-XRD, deconvoluted (b) Ni 2p and (c) B 1s XP spectrum for Ni_xB_y (SR) catalyst after NRR stability tests.

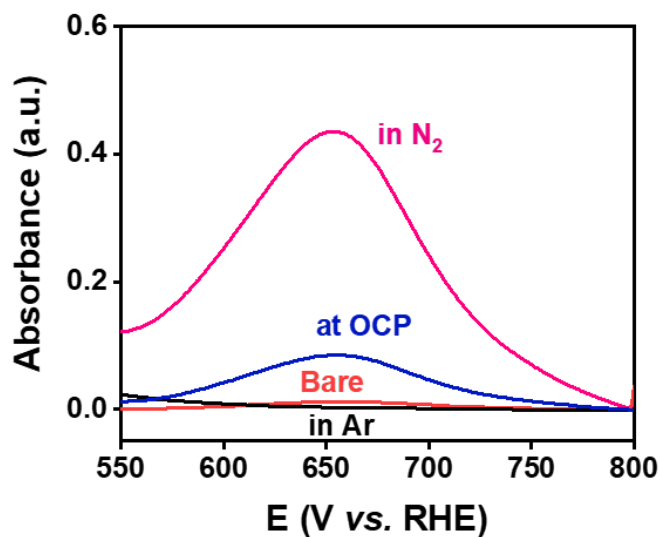


Fig. S8 Control NRR measurements over bare electrode, in Ar-saturated conditions and at open circuit potential depicted by UV-Vis absorbance curves after quantification of ammonia.

Table S3. Comparison of ammonia yield rates after isotope labelling NRR experiments over Ni_xB_y (SR).

Detection method	$^{14}\text{NH}_3$ yield rate ($\text{mg h}^{-1} \text{mg}_{\text{cat.}}^{-1}$)	$^{15}\text{NH}_3$ yield rate ($\text{mg h}^{-1} \text{mg}_{\text{cat.}}^{-1}$)
Indophenol Blue	1.55	1.53
$^1\text{H-NMR}$	1.51	1.5

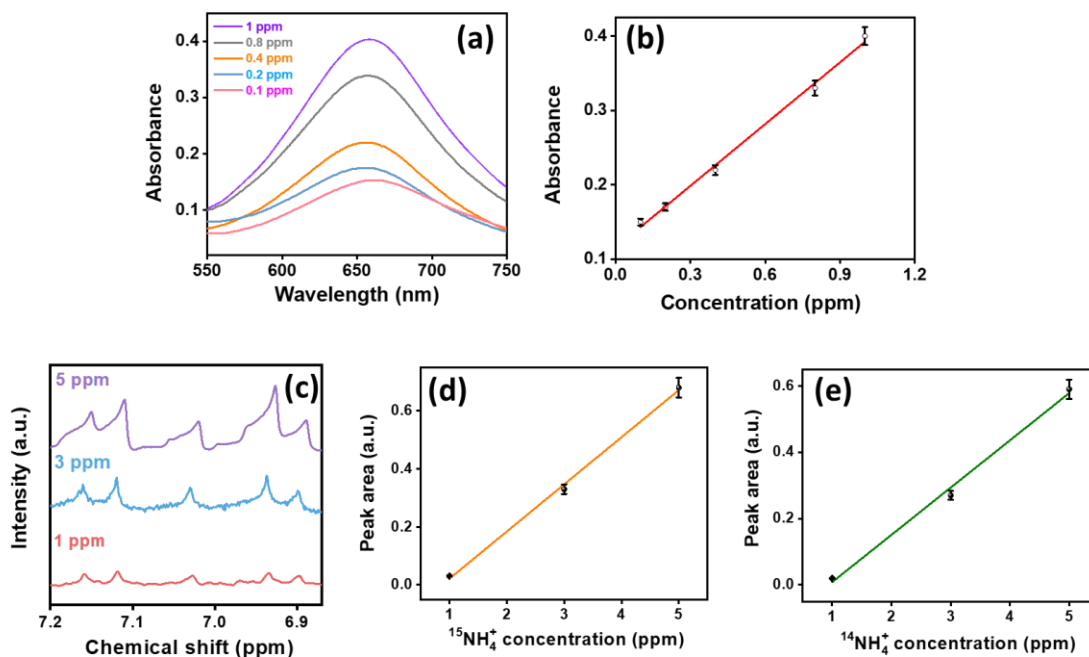


Fig. S9 (a) UV-Vis absorbance curves obtained after Indophenol blue quantification of standard ammonium samples, (b) respective linear calibration curve used for quantification of ammonia in electrolyte samples after NRR. (c) $^1\text{H-NMR}$ spectrum obtained for standard mixture of $^{14}\text{NH}_4^+$ and $^{15}\text{NH}_4^+$ solutions and (d-e) respective calibration curves extracted from the same.

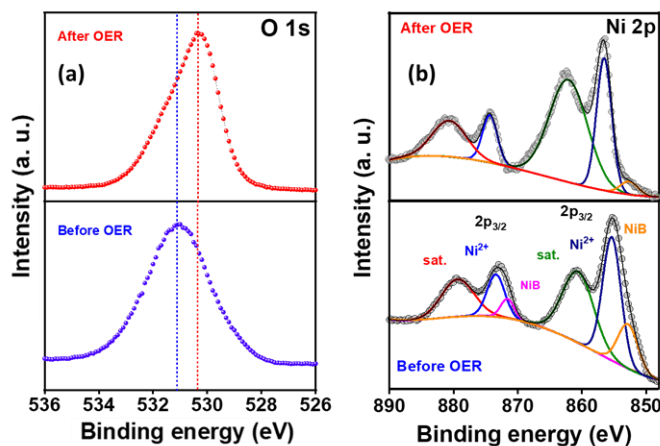


Figure S10. (a) Deconvoluted O 1s XP spectrum and (b) Ni 2p XP spectrum for Ni_xB_y (SR) catalyst before and after OER.

Table S4. Comparison of reported literature for NRR-OER bifunctional catalysts available in literature.

Catalyst	Electrolyte media		Half cell				Full cell (NRR-OER)		Ref.
	Anolyte	Catholyte	OER		NRR		Cell voltage	NH ₄ ⁺ yield rate	
			Overpotential	Tafel slope	Yield rate	F.E.			
CoPi/HSNPC	1 M KOH	0.1 M KOH	341 mV	82 mV dec ⁻¹	16.48 μg h ⁻¹ mg ⁻¹	4.46%	-	-	7
Co _x Fe-MOF	1 M KOH	0.1 M KOH	280 mV	38 mV dec ⁻¹	8.79 μg h ⁻¹ mg ⁻¹	25.64%	-	-	8
CoPi/NPCS	1 M KOH	0.1 M KOH	360 mV	87 mV dec ⁻¹	20.5 μg h ⁻¹ mg ⁻¹	7.07%	-	-	9
I-Co ₃ O ₄	0.1 M KOH	0.1 M K ₂ SO ₄	280 mV	-	5.19 mmol g ⁻¹ h ⁻¹	10.68%	-	-	10
NiFe-nanomesh array	1 M KOH	0.1 M Na ₂ SO ₄	191 mV	43 mV dec ⁻¹	16.89 μg h ⁻¹ mg ⁻¹	12.5%	1.9 V	2.07 μg h ⁻¹ mg ⁻¹	11
MoO ₂ /NF	0.1 M KOH	0.1 M KOH	340 mV	-	9.56 μg h ⁻¹ mg ⁻¹	5.14%	1.7 V	5.73 μg h ⁻¹ mg ⁻¹	12
Ni_xB_y (SR)	0.1 M KOH	0.1 M KOH	300 mV	74.1 mV dec⁻¹	1.55 mg h⁻¹ mg⁻¹	48.9%	1.7 V	1.08 mg h⁻¹ mg⁻¹ (1.9 V)	This work

References

1. L. Zhang, X. Ji, X. Ren, Y. Ma, X. Shi, Z. Tian, A. M. Asiri, L. Chen, B. Tang and X. Sun, *Adv. Mater.*, 2018, **30**, 1800191.
2. A. C. Nielander, J. M. McEnaney, J. A. Schwalbe, J. G. Baker, S. J. Blair, L. Wang, J. G. Pelton, S. Z. Andersen, K. Enemark-Rasmussen and V. Colic, *ACS Catal.*, 2019, **9**, 5797-5802.
3. D. Gupta, A. Kafle, S. Kaur, P. Parimita Mohanty, T. Das, S. Chakraborty, R. Ahuja and T. C. Nagaiah, *J. Mater. Chem. A*, 2022, **10**, 20616-20625.
4. L. Li, C. Tang, D. Yao, Y. Zheng and S.-Z. Qiao, *ACS Energy Lett.*, 2019, **4**, 2111-2116.
5. J. Choi, B. H. Suryanto, D. Wang, H.-L. Du, R. Y. Hodgetts, F. M. Ferrero Vallana, D. R. MacFarlane and A. N. Simonov, *Nat. Commun.*, 2020, **11**, 1-10.
6. D. Gupta, A. Kafle, P. P. Mohanty, T. Das, S. Chakraborty, R. Ahuja and T. C. Nagaiah, *J. Mater. Chem. A*, 2023, **11**, 12223-12235.
7. J.-T. Ren, L. Chen, Y. Liu and Z.-Y. Yuan, *J. Mater. Chem. A*, 2021, **9**, 11370-11380.
8. W. Li, W. Fang, C. Wu, K. N. Dinh, H. Ren, L. Zhao, C. Liu and Q. Yan, *J. Mater. Chem. A*, 2020, **8**, 3658-3666.
9. J.-T. Ren, L. Chen, H.-Y. Wang and Z.-Y. Yuan, *ACS Appl. Mater. Interfaces*, 2021, **13**, 12106-12117.
10. Y. Sun, Q. Wang and Z. Liu, *ACS Appl. Mater. Interfaces*, 2022, **14**, 43508-43516.

11. Y. Sun, T. Jiang, J. Duan, L. Jiang, X. Hu, H. Zhao, J. Zhu, S. Chen and X. Wang, *ACS Catal.*, 2020, **10**, 11371-11379.
12. H.-Y. Wang, J.-T. Ren, C.-C. Weng, X.-W. Lv and Z.-Y. Yuan, *Chem. Eng. J.*, 2021, **426**, 130761.