

Article

Enhanced nitrate-to-ammonia activity on coppernickel alloys via tuning of intermediate adsorption

Yuhang Wang, Aoni Xu, Ziyun Wang, Linsong Huang, Jun Li, Fengwang Li, Joshua Wicks, Mingchuan Luo, Dae-Hyun Nam, Chih-Shan Tan, Yu Ding, Jiawen Wu, Yanwei Lum, Cao-Thang Dinh, David Sinton, Gengfeng Zheng, and Edward H. Sargent

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.9b13347 • Publication Date (Web): 02 Mar 2020 Downloaded from pubs.acs.org on March 2, 2020

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

2 3	4	Enhanced nitrate to ammonic activity on conner nickel alloys
4 5	I	Enhanced intrate-to-animoma activity on copper-incker anoys
6 7 8	2	via tuning of intermediate adsorption
9 10	3	Yuhang Wang ^{†,1} , Aoni Xu ^{†,1} , Ziyun Wang ^{†,1} , Linsong Huang ² , Jun Li ^{1,3} , Fengwang Li ¹ , Joshua
11 12 13	4	Wicks ¹ , Mingchuan Luo ¹ , Dae-Hyun Nam ¹ , Chih-Shan Tan ¹ , Yu Ding ² , Jiawen Wu ² , Yanwei
14 15 16	5	Lum ¹ , Cao-Thang Dinh ¹ , David Sinton ³ , Gengfeng Zheng ² , Edward H. Sargent ^{*,1}
17 18	6	¹ Department of Electrical and Computer Engineering, University of Toronto, 10 King's
19 20 21	7	College Road, Toronto, ON, M5S 3G4, Canada.
22 23 24	8	² Laboratory of Advanced Materials, Department of Chemistry, Fudan University, Shanghai
25 26 27	9	200438, China.
28 29 30	10	³ Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's
31 32	11	College Road, Toronto, ON, M5S 3G8, Canada.
33 34 35 36	12	[†] These authors contributed equally to this work.
37 38 39	13	(*) Correspondence and requests for materials should be addressed to Edward H. Sargent
40 41 42 43 44 45 46 47 48 49 50 51	14	(ted.sargent@utoronto.ca) (E.H.S.)
52 53 54 55 56 57 58 59 60		

15 Abstract

Electrochemical conversion of NO₃⁻ into ammonia (NH₃) recycles nitrogen and offers a route to NH₃ production that is more valuable than dinitrogen gas. However, today's development of NO₃⁻ electroreduction remains hindered by the lack of a mechanistic picture of how catalyst structure may be tuned to enhance catalytic activity. Here we demonstrate enhanced nitrate reduction reaction (NO₃-RR) performance on Cu₅₀Ni₅₀ alloy catalysts, including a 0.12 V upshift in the half-wave potential and a 6-fold increase in activity compared to pure Cu at 0 V vs. reversible hydrogen electrode (RHE). Ni alloying enables tuning of the Cu *d*-band center and modulates the adsorption energies of intermediates such as *NO₃-, *NO₂, and *NH₂. Using density functional theory (DFT) calculations, we identify a NO₃-RR-to-NH₃ pathway and offer an adsorption energy-activity relationship for the CuNi alloy system. This correlation between catalyst electronic structure and NO₃-RR activity offers a design platform for further development of NO₃-RR catalysts.

30 Introduction

Human activities to an anthropogenically-induced increase over time in the concentration of environmental nitrate (NO_3^{-}) :^{1, 2} the combustion of fossil fuels emits nitrous oxides (NO_x) ; fertilizer-intensive agriculture releases NO_3^{-} into soil and groundwater; and NO_3^{-} -containing waste is discharged from industrial sources. The accumulation of NO_3^{-} induces acid rain and photochemical smog^{3, 4} and the uptake of NO_3^{-} in mammals results in its *in vivo* conversion to nitrite (NO_2^{-}) ,^{5, 6} a cause of methemoglobinemia and a known carcinogen.

Closing the nitrate-nitrogen cycle^{1, 2, 7, 8} is therefore of interest: it is desirable to transform
nitrates to harmless⁹⁻¹¹ or – better yet – to value-added products.^{12, 13} The electrochemical
reduction of nitrate provides a route to ammonia production,^{9, 13} with widespread use as a
fertilizer precursor, chemical feedstock and fuel:

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-, E^0 = 0.69 \text{ V vs. RHE } (pH = 14)^{14}$$
 (1)

Achieving higher-performance NO₃-RR electrocatalysts remains challenging, in
significant part because the relationship between catalyst structure and activity is poorly
understood.

To date, Faradaic efficiencies (FE) greater than 90% for NO₃⁻ reduction to NH₃ have been achieved on Cu-based catalysts, but typically these require potentials more negative than -0.27 V vs. RHE in NO₃-containing 1 M KOH electrolytes, corresponding to an overpotential exceeding 0.96 V.¹⁵⁻¹⁹ Previous studies found that alloying Cu with Ni results in a positive shift in the NO₃-RR half-wave potential ($E_{1/2}$), the potential at which the current is equal to one half of the mass transfer limiting current, by $\sim 0.1 \text{ V}$,^{18, 19} a finding that corresponds to enhanced catalytic activity at a given potential. A mechanism wherein Cu performs the adsorption of NO₃* and Ni is the binding site of H* was proposed by Simpson and Johnson;²⁰ however, this

mechanism does not explain enhanced NO₃⁻RR activity on CuNi alloys: Ni converts NO₃⁻ to
NH₃ inefficiently,¹⁹ so that replacing surface Cu atoms with Ni would be expected to reduce
the density of active sites for NH₃ production.

We noted that upshifts in the half-wave potential $(E_{1/2})$ in reduction reactions typically suggest an increase in electrocatalytic activity. This, we posited, could arise due to a modulated intermediate adsorption energy in CuNi alloys compared to pure Cu. Drawing parallels with oxygen reduction reaction (ORR) literature, we noted that platinum-nickel (PtNi) alloy catalysts typically exhibit an upshifted half-wave potential of ~0.1 V compared to pure Pt catalysts.^{21, 22} Decreasing adsorption energies for oxygenated species on PtNi alloys leads to increased activity, an instance of scaling relations for ORR catalysts.²³ This has been associated with the shifted *d*-band center position and surface atomic arrangement reported by Marković and co-workers.²²

In sum, the introduction of heteroatoms modulates the electronic structure of catalysts, enabling the enhancement of electrocatalytic activity.²²⁻²⁵. We explore herein how such a strategy can be employed to design catalysts exhibiting enhanced NO₃-RR activity and selectivity.

We began by preparing a series of CuNi alloys with various Cu:Ni compositions, and
observed a 0.12 V upshift in E_{1/2}, and a 0.2 V lower overpotential required for peak NH₃ FE.
This occurred at a composition - Cu₅₀Ni₅₀ alloy catalysts - that simultaneously produced a 6fold increase in NO₃-RR activity compared to the case of pure Cu at 0 V vs. RHE (pH = 14).
We utilized X-ray photoelectron spectroscopy (XPS), *operando* X-ray adsorption spectroscopy
(XAS) and ultra-violet photoelectron spectroscopy (UPS) to investigate the electronic structure
of the catalysts and found that the Cu *d*-band center upshifted toward the Fermi level in CuNi

alloys. In addition, we investigate the reaction pathway with DFT calculations, and build an
 intermediate adsorption energy-NO₃-RR performance relationship for the CuNi alloy system.

78 Results and discussion

Catalyst synthesis and characterization. We began by electrodepositing catalysts on both rotating disk electrodes (RDEs) and polytetrafluoroethylene (PTFE) membranes covered with 300 nm thick Cu seed layers (300 nm Cu/PTFE). We used electron microscopy to investigate the morphological and crystalline structure of the catalysts. The CuNi catalysts with Cu-to-Ni ratios of 80:20, 50:50, and 30:70 in the deposition solutions, labeled $Cu_{80}Ni_{20}$, Cu₅₀Ni₅₀, and Cu₃₀Ni₇₀, exhibited dendritic morphologies (Fig. 1a, Fig. S1, and S2) with dendrite diameters in the range of 200-400 nm. Using high resolution transmission electron microscopy (HRTEM) we observed lattice spacings of 0.208 and 0.179 nm for the Cu(111) and Cu(200) facets (Fig. 1b) of the Cu₅₀Ni₅₀ catalysts due to the formation of the CuNi alloy phase; compared to pure Cu dendrites exhibiting lattice spacings of 0.210 and 0.181 nm for Cu(111) and Cu(200) facets that agree with cubic Cu (Fig. 1d).²⁶ The Cu-to-Ni ratio in the Cu₅₀Ni₅₀ catalyst, quantified by electron energy loss spectroscopy (EELS, Fig. 1e-h), was ~52:48. We observed similar ratios at other randomly-selected positions (Fig. S3 and Table S1), arguing against a main role for catalyst heterogeneity in catalytic performance. XRD reveals a decrease in Cu lattice spacings when Ni is incorporated (Fig. 1i and S4). The Cu(111) and Cu(100) d-spacings of the $Cu_{50}Ni_{50}$ catalyst revealed by XRD agrees with the results observed with HRTEM.

We also looked for evidence of changes in the electronic properties of the Cu and Cu:Ni
catalysts. XPS indicated a notable decrease in the Cu2p binding energy and an increase in the
metallic Ni2p binding energy for the alloyed catalysts (Fig. 1j and S5). Among the three alloyed
catalysts, we found the largest Cu2p binding energy shift of ~0.35 eV in Cu₅₀Ni₅₀. This can be

explained through electron redistribution²⁷ which leads to an opposite shift of the Cu3d band
toward the Fermi level,²⁸ tuning the adsorption energy of both H* and NO₃*.

In the case of the pure Ni catalysts, only the XRD peaks of the Cu/PTFE support were
observed (Fig. 1i). XPS measurements exhibited a very similar Cu2p binding energy compared
to pristine Cu/PTFE (Fig. S6). SEM, elemental mapping, and Ni2p XPS (Fig. S5 and 7) reveal
only Ni, accompanied by NiO_x formed by oxidation in air, fully covering the Cu/PTFE fibers.

NO₃-RR activity and kinetics. To investigate the electrocatalytic activity and kinetics of NO_3 reduction, we tested each catalyst on rotating disk electrodes (RDEs). With the $Cu_{50}Ni_{50}$ catalyst, we found an onset potential of ~0.25 V vs. RHE (pH = 14) for NO₃⁻ reduction (Fig. 2a). The current density then increased sharply to its transport-limited ceiling of ~170 mA cm⁻² (according to equation 1 in Supporting information) at 100 rpm in 1 M KOH + 100 mM KNO₃ (pH = 14) electrolyte. On the pure Cu catalysts, we found that a much more negative cathodic potential was required to reach this same NO₃⁻-transport-limited current: the current density was only 100 mA cm⁻² at -0.2 V vs. RHE which was only 60% of that obtained by operating the $Cu_{50}Ni_{50}$ catalyst at the same potential. The pure Ni catalyst is almost inactive for NO_3^{-1} reduction (Fig. S8a and b).

The current density, normalized to the electrochemically active surface area (ECSA), increases exponentially to $\sim 1 \text{ mA cm}^{-2}$ along with the cathodic potential for the case of Cu₅₀Ni₅₀. In contrast, an evident multi-electron transfer process (Fig. 2a and b) was seen on the pure Cu catalyst. Cu₅₀Ni₅₀ catalysts exhibited a 40% lower ECSA, determined by its double-layer capacitance, compared to pure Cu (Fig. S9a-c). This translated to a 6-fold increase in ECSAnormalized current density for Cu₅₀Ni₅₀, compared to pure Cu at 0 V vs. RHE (Fig. 2b). The intrinsic NO₃-RR activity was significantly improved using the CuNi alloy systems.

To gain insight into the kinetics, we plotted Koutecký–Levich (K-L) curves for NO₃reduction on the Cu₅₀Ni₅₀ and pure Cu catalysts (Fig. 2c) using their current density vs. potential (*j*-V) profiles in 1 M KOH + 10 mM KNO₃ (pH = 14) electrolyte (Fig. S10 and S8c). K-L analysis revealed a four-electron-transfer process for NH₃ production on both the Cu₅₀Ni₅₀ and Cu catalysts. The kinetic current density obtained using the Cu₅₀Ni₅₀ catalyst was calculated from the intercept of the K-L plot and was 220 mA cm⁻² at -0.25 V vs. RHE, 2x higher than in the case of pure Cu controls (Table S2).

We investigated the $E_{1/2}$ of NO₃-RR on catalysts with different Cu:Ni ratios in 1 M KOH + 10 mM KNO₃ electrolyte. On $Cu_{30}Ni_{70}$, $Cu_{50}Ni_{50}$, $Cu_{80}Ni_{20}$ alloys, we found increasing NO_3^{-1} RR E_{1/2} compared to the pure Cu catalyst. For instance, at 100 rpm, Cu₅₀Ni₅₀ catalyst exhibited the highest $E_{1/2}$ of 0.08 V vs. RHE among all catalysts, while an $E_{1/2}$ of -0.045 V vs. RHE was seen in the case of pure Cu (Fig. S11). The improvement in $E_{1/2}$ further increased to ~120 mV when catalysts were tested in 100 mM KNO₃ at the same rotating rate (Fig. 2a). For all NO₃⁻ concentrations, Cu₅₀Ni₅₀ catalysts perform better than the pure Cu as evidenced by the upshifting of $E_{1/2}$ and the reduced overpotential required for the same current density (Fig. 2d and S7d).

139 NO₃-RR selectivity. We investigated NH₃ selectivity using catalysts deposited on 140 Cu/PTFE supports, *e.g.* the Cu₅₀Ni₅₀ catalyst on PTFE (labeled Cu₅₀Ni₅₀/PTFE), in a flow 141 electrolyzer.²⁹ We quantified the NH₃ product concentration as a function of a range of NO₃⁻ 142 concentrations using an indophenol blue method (Fig. S12). To confirm that the NH₃ produced 143 indeed comes from NO₃⁻ reduction, ¹⁵NO₃⁻ electroreduction was performed using the same 144 catalyst (Fig. S13).

57 145 We achieved a 99 \pm 1% Faradaic efficiency (FE) for NH₃ at ~-0.15 V vs. RHE on the 58 59 146 Cu₅₀Ni₅₀/PTFE catalyst in 1 M KOH + 100 mM KNO₃ electrolyte (Fig. 2e and Table S3). The

> peak FE for NH₃, on Cu₅₀Ni₅₀/PTFE, shifted to a 50 mV lower overpotential compared to that of the pure Cu/PTFE (Fig. S14). The corresponding current density using Cu₅₀Ni₅₀/PTFE was more than 1.3 times higher than that obtained using pure Cu controls (Table. S5). We checked for catalyst reconstruction following NO₃⁻ reduction after a 2-hour NO₃⁻RR operation in 100 mM NO₃⁻ and found that morphologies were retained in the case of both Cu₅₀Ni₅₀/PTFE and pure Cu/PTFE (Fig. S15).

> Alloying with Ni increased the NH₃ FE at low overpotentials (potentials > -0.1 V vs. RHE) in different NO₃⁻ concentrations. Cu₅₀Ni₅₀ catalysts enhanced the NH₃ FE by over 20% at ~0 V vs. RHE compared to pure Cu (Fig. 2f, Table S4 and 5). Specifically, the highest NH₃ FE is $65 \pm 3\%$, $84 \pm 2\%$ and $93 \pm 2\%$ in 1, 2, and 10 mM NO₃⁻ conditions at pH = 14, respectively. In contrast, pure Cu is only able to attain a FE of $42 \pm 3\%$, $59 \pm 3\%$ and $87 \pm 3\%$ at the same NO₃⁻ concentrations.

We achieved a peak NH₃ half-cell energy efficiency (EE) of 40% using Cu₅₀Ni₅₀/PTFE at 50 mA cm⁻² in 100 mM NO₃⁻ (Fig. 2g). This corresponds to a full-cell EE of 31% for this catalyst at 50 mA cm⁻² in the same electrolyte (Fig. S16), which is 1.3-fold improved compared to the case of the pure Cu catalyst. A 31% NH₃ full-cell EE was also obtained using Cu₅₀Ni₅₀/PTFE at 2 mA cm⁻² in 2 mM NO₃⁻ (Fig. S16). This is ~6 times greater than that of the pure Cu catalyst under the same condition.

By studying both the NH₃ FE on Cu₈₀Ni₂₀ and Cu₃₀Ni₇₀ catalysts in 1 mM NO₃⁻, we found that the Cu₅₀Ni₅₀ catalyst was the most active and selective catalyst (Fig. S17 and 18). The NH₃ FE at -0.06 V vs. RHE was $58 \pm 2\%$. Cu₈₀Ni₂₀ catalysts produced NH₃ with a similar FE of 51 ± 2%. Introducing 70% Ni into Cu caused a sharp decrease in NH₃ FE from ~58% to ~31%. Depositing pure Ni largely blocked the Cu sites underneath and further reduced the NH₃ FE to $111 \pm 1\%$.

We implemented the $Cu_{50}Ni_{50}$ catalyst on a 3D porous electrode by depositing the Cu₅₀Ni₅₀ catalyst onto a Cu foam with a pore size of ~200 µm (Fig. S19). We achieved, as a result, a 90 mA cm⁻² current density at -0.1 V vs. RHE, which is two-fold higher than the Cu₅₀Ni₅₀/PTFE electrode in 1 M KOH + 100 M KNO₃ (Fig. 4h). The NH₃ FE was steady at ~95% over 12 h of NO₃-RR and at a 39% NH₃ half-cell energy efficiency (EE). 15% of the input NO₃⁻ was converted into NH₃ in a single pass (Fig. 4h and Table S7).

Electronic structure studies. To shed light on the electronic structure of the CuNi alloy catalysts under NO3⁻RR conditions, we turned to operando hXAS.³⁰ The Cu₅₀Ni₅₀ catalyst in 1 M KOH + 10 mM KNO₃ electrolyte at a series of applied potentials exhibited pure metallic features in both Ni and Cu K-edge spectra under steady-state operation conditions (Fig. 3a-d, Fig. S20). We then calculated the operando coordination numbers (CNs) of Ni at different potentials. The CNs of metal-metal bonds stayed above 11.5 at all potentials (Table S6 and 7). This result suggests that, in our work, there is unlikely to be a prominent role for subsurface oxygen species as previously reported in related catalysts under distinct electrochemical (acidic) conditions.³¹

Since the adsorption energy of intermediates is strongly correlated with the *d*-band center position of catalysts,³² we performed UPS studies for the pure Cu and the CuNi alloys (Fig. 3e). The pure Cu catalyst exhibited a *d*-band center location of -2.84 eV (E-E_F, Fermi level) on the background-corrected spectrum. Increasing the Ni composition in the alloys causes an upshift of the *d*-band center towards the Fermi level by 0.14, 0.28 and 0.32 eV for $Cu_{80}Ni_{20}$, Cu₅₀Ni₅₀ and Cu₃₀Ni₇₀, respectively. These results were in agreement with the XPS results, wherein we observed the 2p electron redistribution which leads to a positive shift of the Cu3d band towards the Fermi level. This indicates decreasing anti-bonding occupation and stronger

adsorbate bonding,³² which means that alloying Ni with Cu greatly enhances the adsorption
energies of intermediate species.

Taken together, the activity, selectivity and *d*-band center positions, allow us to reason that enhanced NO_3 -RR intermediate adsorption, arising due to the shifted *d*-band center position, improved the NO_3 -RR activity and selectivity on CuNi alloys. However, introducing an excess of Ni, *i.e.* the Cu₃₀Ni₇₀ catalyst, reaction intermediates too strongly, which lowers the activity and selectivity.

DFT studies. We sought to investigate, using DFT, the relationship between intermediate 202 adsorption and the NO₃-RR activity of different CuNi catalysts (Fig. 4a). The stability of CuNi 203 alloy systems were screened via doping Ni into Cu at various layers and distributions (Fig. S21, 204 22, and Table S8). Thermodynamics first force Ni atoms to replace the subsurface Cu when 205 the Ni:Cu ratio is less than 1:1. The substitution takes place on Cu surfaces with a further 206 increase in the ratio (Fig. S22).

The electrochemical reaction $NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-$ was represented by a series of deoxidation reactions: $*NO_3^- \rightarrow *NO_2 \rightarrow *NO \rightarrow *N$ followed by hydrogenation reactions of $*N \rightarrow *NH \rightarrow *NH_2 \rightarrow *NH_3$ according to a previous report.³³ With the stable CuNi structures we built, we took different adsorbed orientations of intermediates on all possible active sites into account (Fig. S23 and 24). For all intermediates, the most stable adsorption configurations (Fig. 4a) with the lowest total energies were employed to illustrate the NO₃-RR pathway, and hence assess the activities of different catalysts.

A full NO₃⁻RR pathway in 1 M KOH (pH = 14), including the deoxidation/hydrogenation reactions and intermediates,³³ was then calculated (Fig. 4a). On pure Cu, the first NO₃⁻

adsorption step is the potential-dependent step (PDS) of which the maximum reaction free energy is 0.40 eV at -0.14 V vs. standard hydrogen electrode (SHE). Introducing Ni atoms moves the PDS from NO3⁻ adsorption to the hydrogenation of the *NH2 intermediate (*NH2 + $H_2O + e^- \rightarrow *NH_3 + OH^-$, Figure 4b), as the result of enhanced adsorption caused by the upshifted *d*-band center (Fig. 3e). A volcano-type relationship between the $*NO_3^-$ adsorption energy and the NO₃-RR experimental overpotentials was seen (Fig. 4c). By increasing Ni concentration in CuNi alloys, a stronger adsorption of *NO₃⁻ on the surface further modifies the energetics of NO₃-RR. However, on $Cu_{30}Ni_{70}$ alloy and pure Ni, the reaction free energy for *NH₂ hydrogenation increases to -0.39 and -0.34 eV at -0.14 V vs. SHE, as high Ni fractions lead to *NH₂ intermediate adsorptions exceeding the optimal values. This fact, along with a possible decrease in the number of Cu sites (Fig. S23 and 24), works against the formation of *NH₃ and the selectivity toward NH₃ decreases as a result.

228 Conclusions

This work presents the relationship between intermediate adsorption energies and NO_3^{-1} RR activity on CuNi catalysts. By replacing 50% Cu with Ni, we achieved significantly improved NO₃-RR-to-NH₃ performance. This includes a 0.12 V upshift in the half-wave potential, a 0.2 V lower overpotential required to achieve the optimal NH₃ FE, and a 6-fold increase in NO₃-RR activity on Cu₅₀Ni₅₀ allov catalysts compared to pure Cu at 0 V vs. RHE in alkaline conditions (pH = 14). The electronic structure studies revealed an upshifting of the *d*-band center toward the Fermi level, a feature that enhances intermediate adsorption energies. This relationship was then validated by our DFT calculations, wherein we found that introducing Ni atoms moves the PDS from NO₃⁻ adsorption to *NH₂ hydrogenation due to the enhanced adsorption energy of NO₃⁻ on the CuNi surface, and as a result, lowers the overpotential. Our work demonstrates the effect of the *d*-band center positions and the induced

4
5
6
7
, Q
0
9
10
11
12
13
14
15
16
17
17
18
19
20
21
22
23
24
24
25
26
27
28
29
30
31
37
22
33
34
35
36
37
38
39
10
40 // 1
41
42
43
44
45
46
47
48
40 40
49
50
51
52
53

adsorption properties on the NO₃-RR activity and selectivity. This work highlights a promising

route to design catalysts for selective NO₃-RR to NH₃.

242	Acknowledgements
-----	------------------

This work was financially supported by the Ontario Research Fund: Research Excellence Program, the Natural Sciences and Engineering Research Council (NSERC) of Canada, and the CIFAR Bio-Inspired Solar Energy program. This research used synchrotron resources of the Advanced Photon Source (APS), an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, and was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357, and the Canadian Light Source and its funding partners. All DFT computations were performed on the IBM BlueGene/Q supercomputer with support from the Southern Ontario Smart Computing Innovation Platform (SOSCIP) and Niagara supercomputer at the SciNet HPC Consortium. SOSCIP is funded by the Federal Economic Development Agency of Southern Ontario, the Province of Ontario, IBM Canada Ltd., Ontario Centres of Excellence, Mitacs and 15 Ontario academic member institutions. SciNet is funded by: the Canada Foundation for Innovation; the Government of Ontario; Ontario Research Fund - Research Excellence; and the University of Toronto. We acknowledge the Toronto Nanofabrication Centre (TNFC) and the Ontario Centre for the Characterization of Advanced Materials (OCCAM) for sample preparation and characterization facilities. The authors thank Dr. T. P. Wu, and L. Ma for technical support at 9BM beamline of APS. D.S. acknowledges the NSERC E.W.R Steacie Memorial Fellowship. J.L. acknowledges the Banting postdoctoral fellowship from Govt. of Canada.

⁰ 261

262 Supplementary materials

- 263 Materials and Methods
- 264 Figs. S1 to S24
- 5 265 Tables S1 to S8

2		
3	267	Competing financial interests: The authors declare no competing financial interests.
4 5		
6	268	
7		
8	269	Data and materials availability
9 10		
11	270	All data are reported in the main text and supplementary materials.
12		1 11 2
13	074	
14	271	
16		
17		
18 10		
20		
21		
22		
23 24		
25		
26		
27		
28 29		
30		
31		
32		
33 34		
35		
36		
37		
38 39		
40		
41		
42		
43 44		
45		
46		
4/ 48		
49		
50		
51 52		
52 53		
54		
55		
56 57		
57		
59		
60		14
		± •





Figure 1. Materials characterization of copper-nickel alloy catalysts. (a, b) Representative
SEM and HRTEM images of the Cu₅₀Ni₅₀ catalyst. (c, d) Representative SEM and HRTEM
images of the pure Cu catalyst. The scale bars are 200 nm in a and c, and 10 nm in b and d.
(e-h) The STEM image and EELS mapping analysis of the Cu₅₀Ni₅₀ catalyst. The scale bars
are 100 nm. (i, j) XRD patterns and XPS Cu2p spectra of catalysts with different Cu:Ni ratios.



Figure 2. Nitrate-to-ammonia electroreduction performance. (a) j-V plots of nitrate reduction (80% *iR* corrected) on the Cu₅₀Ni₅₀, pure Cu and pure Ni RDE at 100 rpm in 1 M KOH + 0.1 M KNO₃ electrolyte. (b) ECSA-normalized current densities. (c) Koutecký–Levich plots of nitrate reduction on Cu₅₀Ni₅₀ and Cu at -0.25 V vs. RHE in 1 M KOH + 10 mM KNO₃ electrolyte. (d) *j*-V plots of nitrate reduction (80% *iR* corrected) on the Cu₅₀Ni₅₀ RDE at 400 rpm. (e) Nitrate-to-ammonia Faradaic efficiency on the Cu₅₀Ni₅₀/PTFE catalyst in different nitrate concentrations. (f) Comparison of the highest NH₃ Faradaic efficiency on the $Cu_{50}Ni_{50}/PTFE$ and pure Cu/PTFE catalysts in different nitrate concentrations. (g) Comparison of the cathodic (half-cell) NH₃ energy efficiency (EE) obtained using the Cu₅₀Ni₅₀/PTFE and pure Cu/PTFE catalysts. (h) Stability and single-pass conversion test of nitrate reduction at -0.1 V vs. RHE using a Cu₅₀Ni₅₀/Cu foam catalyst.



Figure 3. Electronic structure. (a) *Operando* Cu K-edge hXAS spectra of the $Cu_{50}Ni_{50}$ catalyst at different applied potentials. (b) Fourier-transformed *operando* Cu K-edge hXAS spectra of the $Cu_{50}Ni_{50}$ catalyst at different applied potentials. (c) *Operando* Ni K-edge hXAS spectra of the $Cu_{50}Ni_{50}$ catalyst at different applied potentials. (d) Fourier-transformed *operando* Ni K-edge hXAS spectra of the $Cu_{50}Ni_{50}$ catalyst at different applied potentials. (d) Fourier-transformed *operando* Ni K-edge hXAS spectra of the $Cu_{50}Ni_{50}$ catalyst at different applied potentials. (e) The UPS spectra and *d*-band center positions of pure Cu catalysts and the CuNi alloys.



Figure 4. DFT calculations. (a) Reaction free energies for different intermediates on CuNi
surface. (b). Hydrogenation reaction of *NH₂ (*NH₂ + H₂O + e⁻ → *NH₃ +OH⁻) on Cu₃₀Ni₇₀
surface. (c) The volcano-type relationship between experimental overpotentials of NO₃ RR at
5 mA cm⁻² in 10 mM KNO₃ and adsorption energies of *NO₃⁻ on all CuNi alloys. Red, pink,
blue, grey and orange spheres correspond to oxygen, hydrogen, nitrogen, nickel and copper
atoms, respectively.

1 2 3 4	308	Reference	es
6 7	309	1.	N. Gruber, J. N. Galloway. An Earth-system perspective of the global nitrogen cycle.
8 9	310		<i>Nature</i> 2008 , 451, 293-296.
10 11 12	311	2.	D. E. Canfield, A. N. Glazer, P. G. Falkowski. The evolution and future of Earth's
12 13 14	312		nitrogen cycle. Science 2010, 330, 192-196.
15 16 17 18 19	313	3.	Penn State. Clean air act reduces acid rain in eastern United States. ScienceDaily
	314		September 28, 1998,
19 20 21	315	4.	NO _x /VOC office. <i>NO_x/VOC somg fact sheet</i> . Canadian Council of Ministers of the
22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39	316		Environment. Ottawa, ON, Canada, 1998.
	317	5.	M. J. Moorcroft, J. Davis, R. G. Compton. Detection and determination of nitrate
	318		and nitrite: a review. Talanta 2001, 54, 785-803.
	319	6.	B. T. Nolan, K. J. Hitt, B. C. Ruddy. Probability of nitrate contamination of recently
	320		recharged groundwaters in the conterminous United States. Environ. Sci. Technol.
	321		2002 , 36, 2138-2145.
	322	7.	M. Ascott, D. C. Gooddy, L. Wang, M.E. Stuart, M. A. Lewis, R. S. Ward, A. M.
	323		Binley. Global patterns of nitrate storage in the vadose zone. Nat. Commun. 2017,
40 41 42	324		8, 1416.
42 43 44	325	8.	C. L. Ford, Y. J. Park, E. M. Matson, Z. Gordon, A. R. Fout. A bioinspired iron
45 46	326		catalyst for nitrate and perchlorate reduction. Science 2016, 354, 741-743.
47 48 40	327	9.	M. Duca, M. T. Koper. Powering denitrification: the perspectives of electrocatalytic
49 50 51	328		nitrate reduction. Energy Environ. Sci. 2012, 5, 9726-9742.
52 53	329	10.	V. Rosca, M. Duca, M. T. de Groot, M. T. Koper. Nitrogen cycle electrocatalysis.
54 55	330		Chem. Rev. 2009, 109, 2209-2244.
50 57 58	331	11.	S. Seraj, P. Kunal, H. Li, G. Henkelman, S. M. Humphrey, C. J. Werth. PdAu alloy
59 60	332		nanoparticle catalysts: effective candidates for nitrite reduction in water. ACS Catal. 19

2			
3 4	333		2017, 7, 3268-3276.
5 6	334	12.	D. P. Butcher, A. A. Gewirth. Nitrate reduction pathways on Cu single crystal
/ 8 0	335		surfaces: Effect of oxide and Cl ⁻ . Nano Energy 2016, 29, 457-465.
10 11 12 13 14 15 16	336	13.	E. Pérez-Gallent, M. C. Figueiredo, I. Katsounaros, M. T. Koper. Electrocatalytic
	337		reduction of nitrate on copper single crystals in acidic and alkaline solutions.
	338		<i>Electrochim. Acta</i> 2017, 227, 77-84.
16 17 18	339	<mark>14.</mark>	J. G. Chen, R. M. Crooks, L. C. Seefeldt, K. L. Bren, R. M. Bullock, M. Y.
19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40	340		Darensbourg, P. L. Hooand, B. Hoffman, M. J. Janik, A. K. Jones, M. G. Kanatzidis,
	341		P. King, K. M. Lancaster, S. V. Lymar, P. Pfromm, W. F. Schneider, R. R. Schrock.
	342		Beyond fossil fuel-driven nitrogen transformations. Science 2018, 360, eaar6611.
	343	15.	D. Reyter, G. Chamoulaud, D. Bélanger, L. Roué. Electrocatalytic reduction of
	344		nitrate on copper electrodes prepared by high-energy ball milling. J. Electroanal.
	345		<i>Chem.</i> 2006, 596, 13-24.
	346	16.	D. Reyter, D. Bélanger, L. Roué. Study of the electroreduction of nitrate on copper
	347		in alkaline solution. Electrochim. Acta 2008, 53, 5977-5984.
	348	17.	N. Comisso, S. Cattarin, S. Fiameni, R. Gerbasi, L. Mattarozzi, M. Musiani, L.
	349		Vázquez-Gómez, E. Verlato. Electrodeposition of Cu-Rh alloys and their use as
42 43	350		cathodes for nitrate reduction. <i>Electrochem. Commun.</i> 2012, 25, 91-93.
44 45	351	18.	L. Mattarozzi, S. Cattarin, N. Comisso, A. Gambirasi, P. Guerriero, M. Musiani, L.
46 47	352		Vázquez-Gómez, E. Verlato. Hydrogen evolution assisted electrodeposition of
49 50	353		porous Cu-Ni alloy electrodes and their use for nitrate reduction in alkali.
51 52	354		<i>Electrochim. Acta</i> 2014, 140, 337-344.
53 54	355	19.	L. Mattarozzi, S. Cattarin, N. Comisso, P. Guerriero, M. Musiani, L. Vázquez-
55 56 57	356		Gómez, E. Verlato. Electrochemical reduction of nitrate and nitrite in alkaline
59 59	357		media at CuNi alloy electrodes. Electrochim. Acta 2013, 89, 488-496.
60			

1 2			
3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25	358	20.	B. K. Simpson, D. C. Johnson. Electrocatalysis of nitrate reduction at copper-nickel
	359		alloy electrodes in acidic media. <i>Electroanalysis</i> . 2004, 16, 532-538.
	360	21.	V. R. Stamenković, T. J. Schmidt, P. N. Ross, N. M. Marković. Surface composition
	361		effects in electrocatalysis: kinetics of oxygen reduction on well-defined Pt ₃ Ni and
	362		Pt ₃ Co alloy surfaces. J. Phys. Chem. B 2002, 106, 11970-11979.
	363	22.	V. R. Stamenković, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas, N.
	364		M. Marković. Improved oxygen reduction activity on Pt ₃ Ni(111) via increased
	365		surface site availability. Science 2007, 315, 493-499.
	366	23.	J. K. Nørskow, J. Rossmeisl, A. Logadottir, L. Lindqvist. Origin of the overpotential
	367		for oxygen reduction at a fuel-cell cathode. J. Phys. Chem. B 2004, 108, 17886-
26 27	368		17892.
28 29	369	24.	H. Huang, H. Jia, Z. Liu, P. Gao, J. Zhao, Z. Luo, J. Yang, J. Zeng. Understanding
30 31 32	370		of strain effects in the electrochemical reduction of CO ₂ : using Pd nanostructures
33 34	371		as an ideal platform. Angew. Chem. Int. Ed. 2017, 56, 3594-3598.
35 36	372	25.	D. Kim, J. Resasco, Y. Yu, A. M. Asiri, P. Yang. Synergistic geometric and
37 38	373		electronic effects for electrochemical reduction of carbon dioxide using gold-
39 40 41	374		copper bimetallic nanoparticles. Nat. Commun. 2014, 5, 4948.
42 43	375	26.	T. Theivasanthi, M. Alagar. X-ray diffraction studies of copper nanopowder. 2010,
44 45	376		arXiv preprint arXiv:1003.6068.
46 47 48	377	27.	A. Jha, DW. Jeong, JO. Shim, WJ. Jang, YL. Lee, C. V. Rode, HS. Roh.
49 50	378		Hydrogen production by the water-gas shift reaction using CuNi/Fe ₂ O ₃ catalyst.
51 52	379		Catal. Sci. Technol. 2015, 5, 2752-2760.
53 54 55	380	28.	H. H. Hsieh, Y. K. Chang, W. F. Pong, J. Y. Pieh, P. K. Tseng, TK. Sham, I.
56 57	381		Couthard, S. J. Naftel, J. F. Lee, S. C. Chung, K. L. Tsang. Electronic structure of
58 59	382		Ni-Cu alloys: the <i>d</i> -electron charge distribution. Phys. Rev. B 1998, 57, 15204-
60			21

- - 15210.
 - 29. C.-T. Dinh, T. Burdyny, M. G. Kibria, A. Seifitokaldani, C. M. Gabardo, F. P. G.
 385 de Arquer, A. Kiani, J. P. Edwards, P. De Luna, O. S. Bushuyev, C. Zou, R.
 386 Quintero-Bermudez, Y. Pang, D. Sinton, E. H. Sargent. CO₂ electroreduction to
 a87 ethylen via hydroxide-mediated copper catalysis at an abrupt interface. *Science*388 2018, 360, 783-787.
- 389 30. J. Li, F. Che, Y. Pang, C. Zou, J. Y. Howe, T. Burdyny, J. P. Edwards, Y. Wang,
 390 F. Li, Z. Wang, P. De Luna, C.-T. Dinh, T.-T. Zhuang, M. I. Saidaminov, S. Cheng,
 391 T. Wu, Y. Z. Finfrock, L. Ma, S.-H. Hsieh, Y.-S. Liu, G. A. Botton, W.-F. Pong, X.
 392 Du, J. Guo, T.-K. Sham, E. H. Sargent, D. Sinton. Copper adparticle enabled
 selective electrosynthesis of n-propanol. *Nat. Commun.* 2018, 9, 4614.
 - 394 31. S.-E. Bae, K. L. Stewart, A. A. Gewirth. Nitrate adsorption and reduction on Cu(100)
 in acidic solution. J. Am. Chem. Soc. 2007, 129, 10171-10180.
 - 396 32. J. K. Nørskov, F. Abild-Pedersen, F. Studt, T. Bligaard. Density functional theory
 397 in surface chemistry and catalysis. *Proc. Natl. Acad. Sci.* 2011, 108, 937-943.
 - 398 33. J.-X. Liu, D. Richards, N. Singh, B. R. Goldsmith. Activity and Selectivity Trends
 in electrocatalytic nitrate reduction on transition metals. *ACS Catal.* 2019, 9, 7052400 7064.







Figure 1. Materials characterization of copper-nickel alloy catalysts. (a, b) Representative SEM and HRTEM images of the Cu₅₀Ni₅₀ catalyst. (c, d) Representative SEM and HRTEM images of the pure Cu catalyst. The scale bars are 200 nm in a and c, and 10 nm in b and d. (e-h) The STEM image and EELS mapping analysis of the Cu₅₀Ni₅₀ catalyst. The scale bars are 100 nm. (i, j) XRD patterns and XPS Cu₂p spectra of catalysts with different Cu:Ni ratios.



Figure 2. Nitrate-to-ammonia electroreduction performance. (a) *j*-*V* plots of nitrate reduction (80% *iR* corrected) on the Cu₅₀Ni₅₀, pure Cu and pure Ni RDE at 100 rpm in 1 M KOH + 0.1 M KNO₃ electrolyte. (b) ECSA-normalized current densities. (c) Koutecký-Levich plots of nitrate reduction on Cu50Ni50 and Cu at - 0.25 V vs. RHE in 1 M KOH + 10 mM KNO₃ electrolyte. (d) *j*-V plots of nitrate reduction (80% *iR* corrected) on the Cu₅₀Ni₅₀ RDE at 400 rpm. (e) Nitrate-to-ammonia Faradaic efficiency on the Cu50Ni50/PTFE catalysts in different nitrate concentrations. (f) Comparison of the highest NH₃ Faradaic efficiency on the Cu₅₀Ni₅₀/PTFE and pure Cu/PTFE catalysts in different nitrate concentrations. (g) Comparison of the cathodic (half-cell) NH₃ energy efficiency (EE) obtained using the Cu₅₀Ni₅₀/PTFE and pure Cu/PTFE catalysts. (h) Stability and single-pass conversion test of nitrate reduction at -0.1 V vs. RHE using a

Cu₅₀Ni₅₀/Cu foam catalyst.



Figure 3. Electronic structure. (a) *Operando* Cu K-edge hXAS spectra of the Cu₅₀Ni₅₀ catalyst at different applied potentials. (b) Fourier-transformed *operando* Cu K-edge hXAS spectra of the Cu₅₀Ni₅₀ catalyst at different applied potentials. (c) *Operando* Ni K-edge hXAS spectra of the Cu₅₀Ni₅₀ catalyst at different applied potentials. (d) Fourier-transformed *operando* Ni K-edge hXAS spectra of the Cu₅₀Ni₅₀ catalyst at different applied potentials. (e) The UPS spectra and *d*-band center positions of pure Cu catalysts and the CuNi alloys.



60



Figure 4. DFT calculations. (a) Reaction free energies for different intermediates on CuNi surface. (b). Hydrogenation reaction of *NH₂ (*NH₂ + H₂O + $e^- \rightarrow *NH_3 + OH^-$) on Cu₃₀Ni₇₀ surface. (c) The volcanotype relationship between experimental overpotentials of NO₃⁻RR at 5 mA cm⁻² in 10 mM KNO₃ and adsorption energies of *NO₃⁻ on all CuNi alloys. Red, pink, blue, grey and orange spheres correspond to oxygen, hydrogen, nitrogen, nickel and copper atoms, respectively.