First-Principles Simulations of Ni-based Materials for Electrochemical Ammonia Oxidation

Celebrating Jens Nørskov's 70th Birthday

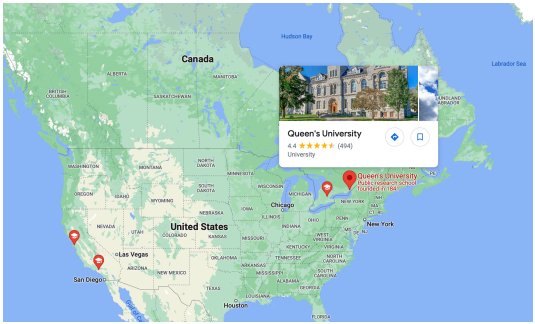
Leanne Chen

September 12, 2022

University of Guelph

ELECTROCHEMICAL TECHNOLOGY CENTRE
DEPARTMENT OF CHEMISTRY

My Academic Journey

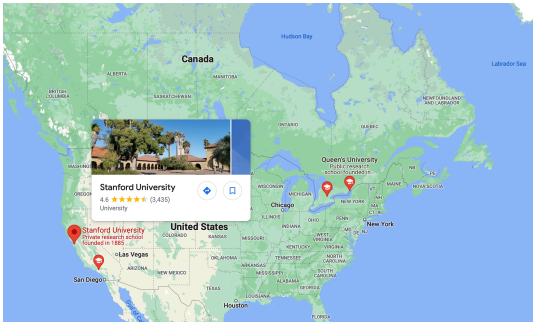


BScH: Queen's University (2008–2012)

Nick Mosey and Suning Wang†

DFT mechanistic investigations of photochromic organoboron compounds

My Academic Journey

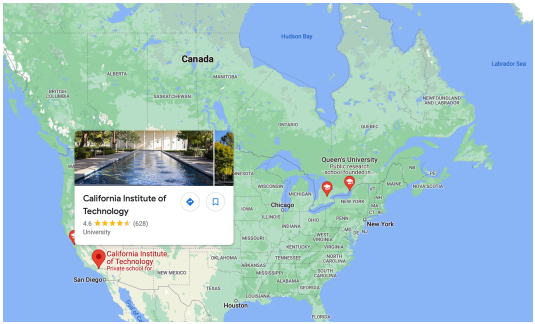


PhD: Stanford University (2012–2017)

Jens Nørskov

DFT studies of electrochemical and electrocatalytic systems

My Academic Journey

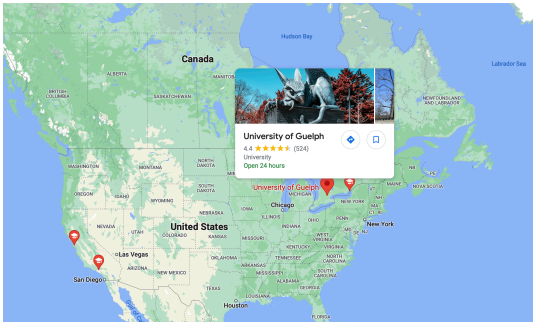


Postdoctoral Scholar: Caltech (2017–2019)

Tom Miller

QM/MM MD simulations of homogeneous catalysts

My Academic Journey



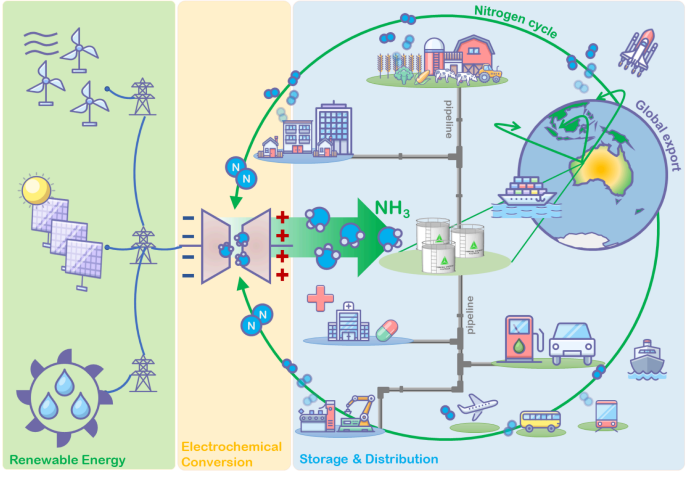
Independent Career: University of Guelph (2020–present)

Rachelle Choueiri, PhD 2016
University of Toronto (Eugenia Kumacheva)
Postdoctoral Fellow

Memories of SUNCAT

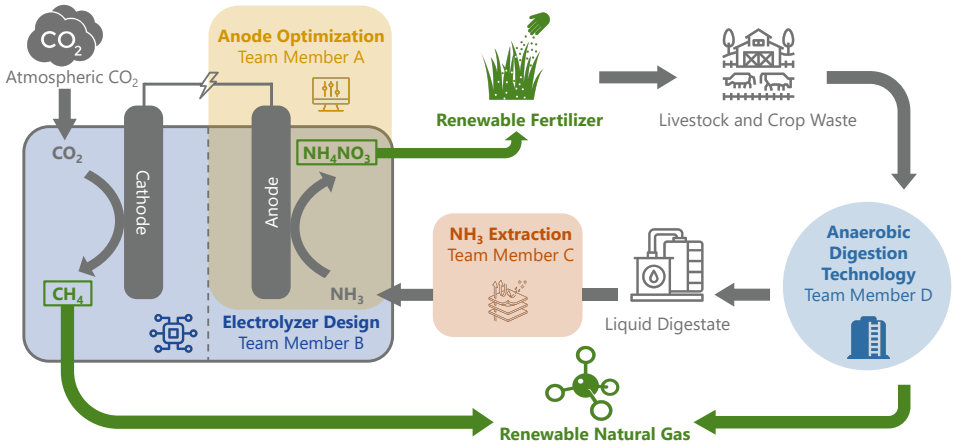
SUNCAT Theory + Experiment, taken at SLAC (2013?)

The Ammonia Economy



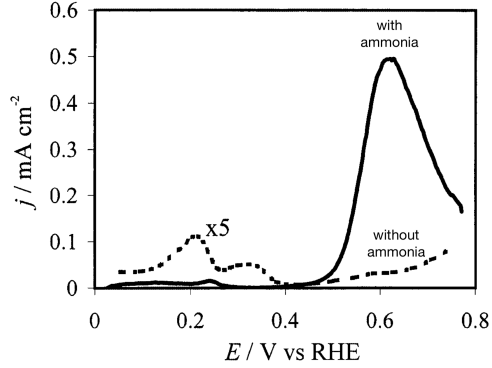
MacFarlane, D. R.; Cherepanov, P. V.; Choi, J.; Suryanto, B. H. R.; Hodgetts, R. Y.; Bakker, J. M.; Ferrero Vallana, F. M.; Simonov, A. N. *Joule* **2020**, *4*, 1186–1205.

Why Study Ammonia Oxidation at All?

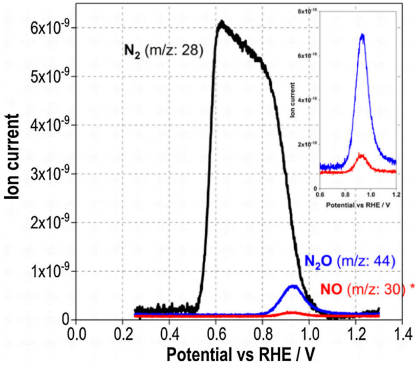


L. D. Chen, New Frontiers for Research Fund

NH_3 Oxidation on Pt

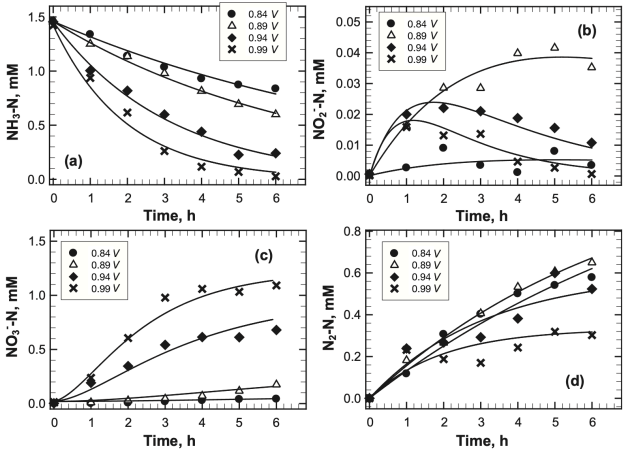


de Vooys, A. C. A.; Koper, M. T. M.; van Santen, R. A.; van Veen, J. A. R. *Electroanal. Chem.* **2001**, *506*, 127–137.



Katsounaros, I.; Figueiredo, M. C.; Calle-Vallejo, F.; Li, H.; Gewirth, A. A.; Marković, N. M.; Koper, M. T. M. *J. Catal.* **2018**, *359*, 82–91.

NH_3 Oxidation on NiO_xH_y



Shih, Y.-J.; Huang, Y.-H.; Huang, C. P. *Electrochim. Acta.* **2018**, *263*, 261–271.

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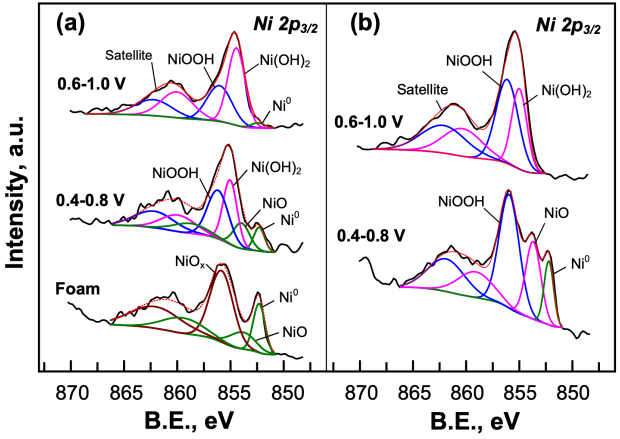
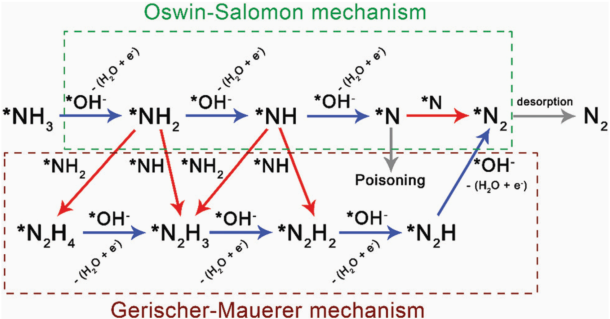


Shih, Y.-J.; Huang, Y.-H.; Huang, C. P. *Electrochim. Acta.* **2018**, *263*, 261–271.

NH_3 Oxidation Mechanisms



Guo, W.; Zhang, K.; Liang, Z.; Zou, R.; Xu, Q. *Chem. Soc. Rev.* **2019**, *48*, 5658–5716.

Our goal: map out the O-S and G-M mechanisms for N_2 formation on $Ni(OH)_2$ and NiOOH, and propose new mechanisms for the production of NO_2^- and NO_3^- (previously unknown).

Our Proposed Mechanism

Steps considered in pathway toward dinitrogen formation:

$$NH_3(g) + OH^-(aq) + * \rightarrow *NH_2 + H_2O(l) + e^-$$
$$*NH_2 + OH^-(aq) \rightarrow *NH + H_2O(l) + e^-$$
$$*NH + OH^-(aq) \rightarrow *N + H_2O(l) + e^-$$
$$*NH_2 + *NH_2 \rightarrow *NH_2\text{-}NH_2$$
$$*NH + *NH \rightarrow *NH\text{-}NH$$
$$*NH\text{-}NH + OH^-(aq) \rightarrow *N\text{-}NH + H_2O(l) + e^-$$
$$*N + *NH \rightarrow *N\text{-}NH$$
$$*N\text{-}NH + OH^-(aq) \rightarrow *N\text{-}N + H_2O(l) + e^-$$
$$*N + *N \rightarrow *N\text{-}N$$
$$*N\text{-}N \rightarrow N_2(g) + *$$

Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *Electro. Chem. Sci. Adv.* **2021**, 2100142.

Our Proposed Mechanism

Additional steps considered for nitrite formation:

$$^*NH_2 + OH^-(aq) \rightarrow {}^*NH_2OH + e^-$$
$$^*NH + OH^-(aq) \rightarrow {}^*NHOH + e^-$$
$$^*N + OH^-(aq) \rightarrow {}^*NOH + e^-$$
$$^*NOH + OH^-(aq) \rightarrow {}^*NO + H_2O(l) + e^-$$
$$^*NO + OH^-(aq) \rightarrow {}^*NO_2H + e^-$$
$$^*NO_2H + OH^-(aq) \rightarrow NO_2{}^-(aq) + H_2O(l) + {}^*$$

Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *Electro. Chem. Sci. Adv.* **2021**, 2100142.

Our Proposed Mechanism

Additional steps considered for nitrate formation:

$$^*NO_2H + OH^-(aq) \rightarrow {}^*NO_2 + H_2O(l) + e^-$$
$$^*NO_2 + OH^-(aq) \rightarrow {}^*NO_3H + e^-$$
$$^*NO_3H + OH^-(aq) \rightarrow NO_3^-(aq) + H_2O(l) + {}^*$$

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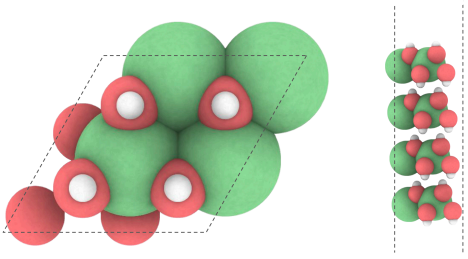
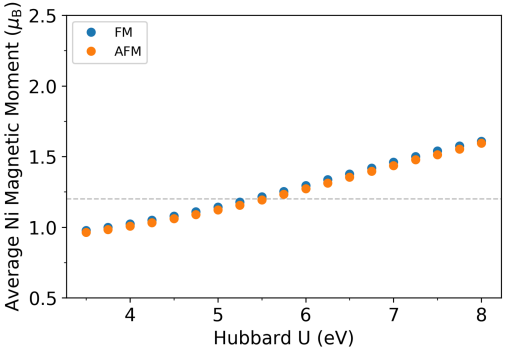
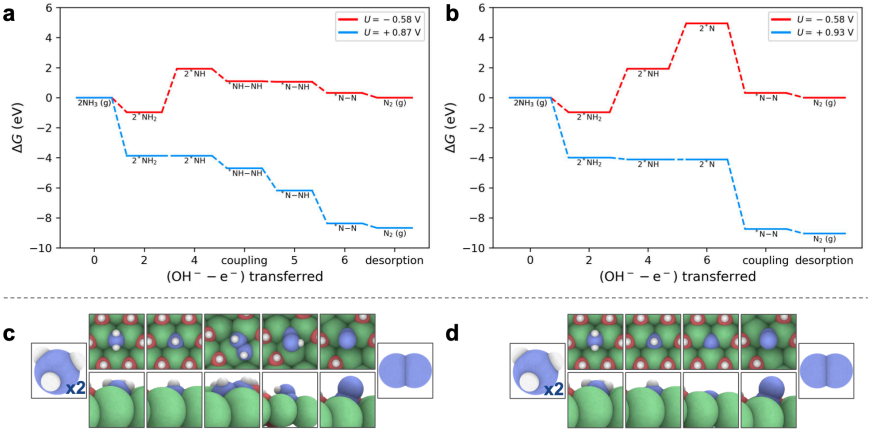
Simulating β-Ni(OH)$_2$





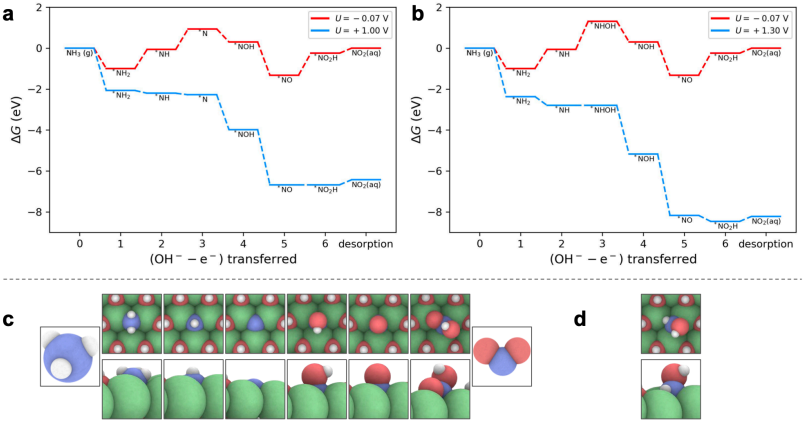
Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *Electro. Chem. Sci. Adv.* **2021**, 2100142.

Formation of N_2 on β-$Ni(OH)_2$



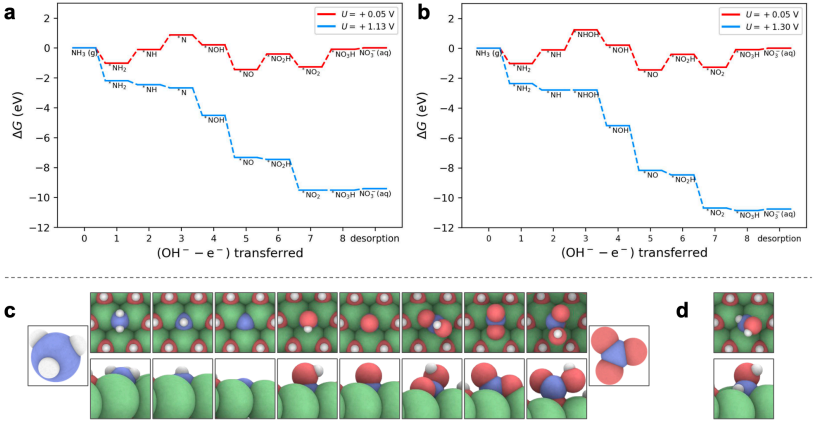
Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *Electro. Chem. Sci. Adv.* **2021**, 2100142.

Formation of NO_2^- on β-$Ni(OH)_2$



Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *Electro. Chem. Sci. Adv.* **2021**, 2100142.

Formation of NO_3^- on β-$Ni(OH)_2$



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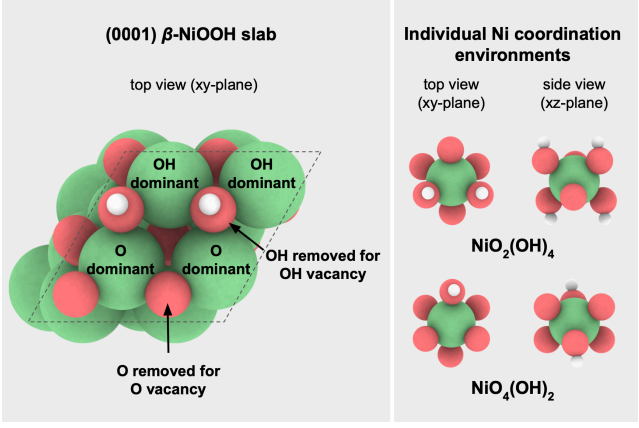
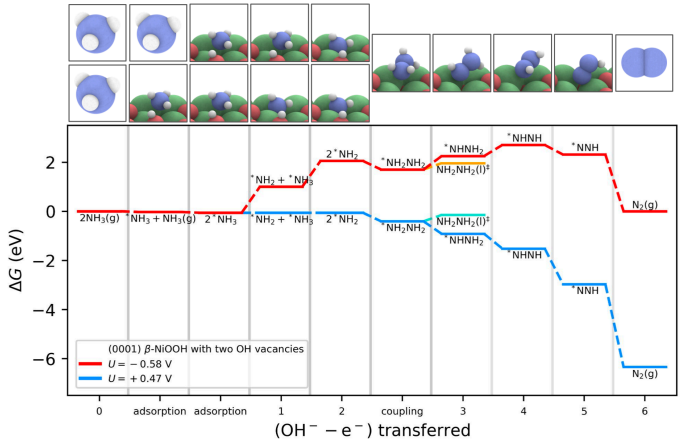
Structure of β-NiOOH



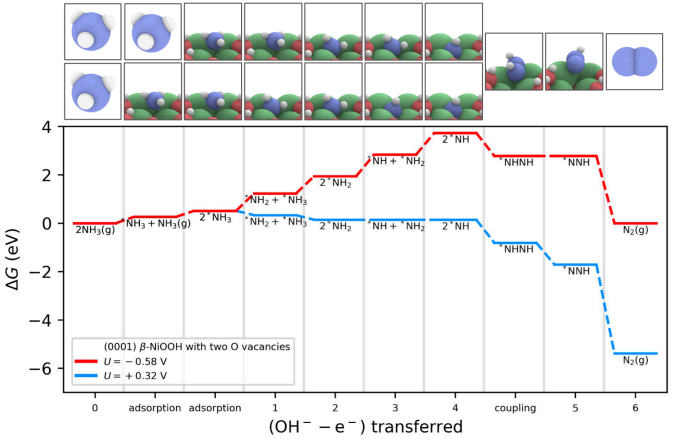
Choueiri, R. M. and Chen, L. D. *ChemRxiv* **2022**, Preprint.

Formation of N_2 on β-NiOOH with Two OH Vacancies



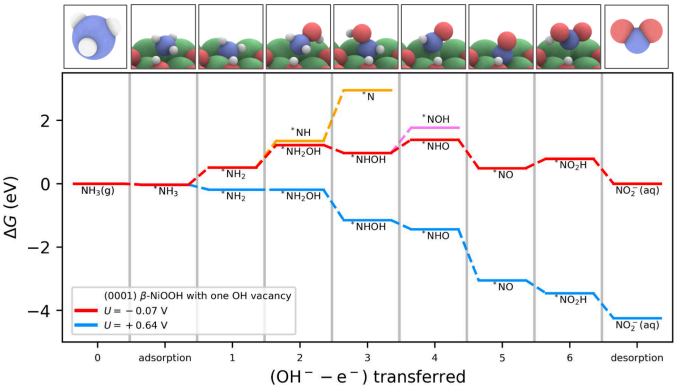
Choueiri, R. M. and Chen, L. D. *ChemRxiv* **2022**, Preprint.

Formation of N_2 on β-NiOOH with Two O Vacancies



Choueiri, R. M. and Chen, L. D. *ChemRxiv* **2022**, Preprint.

Formation of NO_2^- on β-NiOOH with an OH Vacancy



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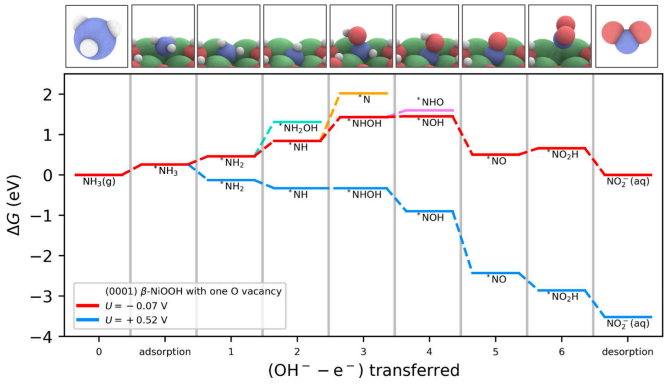

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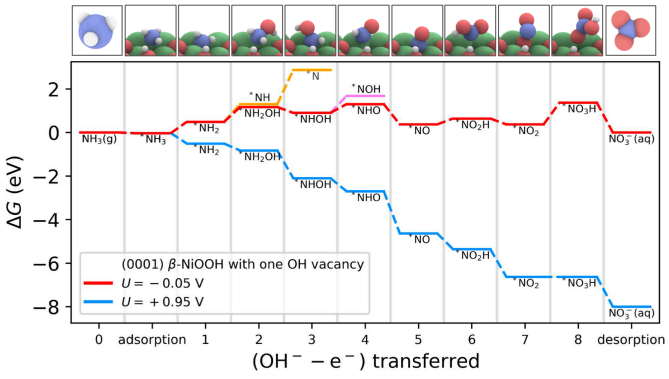

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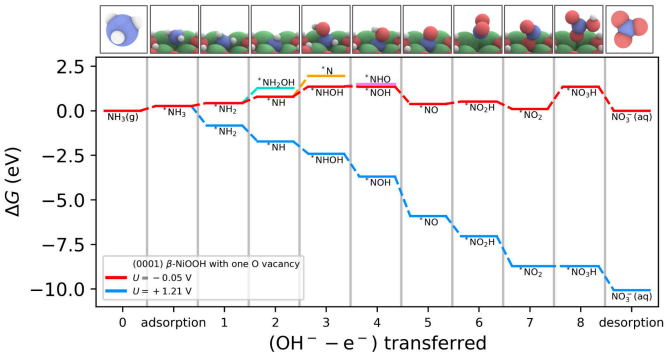
Formation of NO_3^- on β-NiOOH with an O Vacancy



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Comparison between β-Ni(OH)$_2$ and β-NiOOH

Slab	U_{limiting} (V_{SHE})	Pathway	Limiting Step
Dinitrogen formation			
β-Ni(OH)$_2$	+0.87	NH-NH coupling	$^*NH_2 \rightarrow ^*NH$
OH/OH	+0.47	NH_2-NH_2 coupling	$^*NH_3 \rightarrow ^*NH_2$
O/O	+0.32	NH-NH coupling	$^*NH_2 \rightarrow ^*NH$
Nitrite formation			
β-Ni(OH)$_2$	+1.00	*via* $^*N$	$^*NO \rightarrow ^*NO_2H$
OH	+0.64	*via* $^*NH_2OH$	$^*NH_2 \rightarrow ^*NH_2OH$
O	+0.52	*via* $^*NHOH$	$^*NH \rightarrow ^*NHOH$
Nitrate formation			
β-Ni(OH)$_2$	+1.13	*via* $^*N$	$^*NO_2 \rightarrow ^*NO_3H$
OH	+0.95	*via* $^*NH_2OH$	$^*NO_2 \rightarrow ^*NO_3H$
O	+1.21	*via* $^*NHOH$	$^*NO_2 \rightarrow ^*NO_3H$

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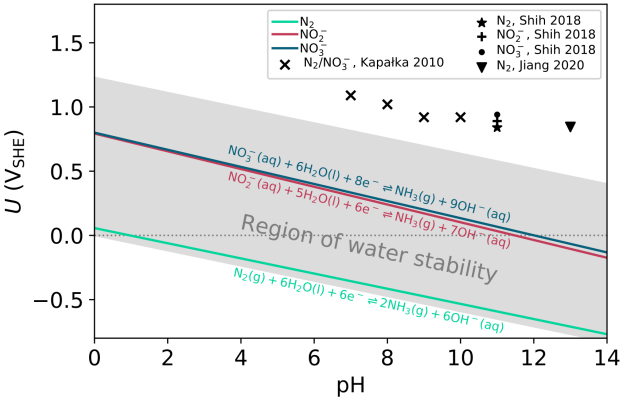
Ammonia Oxidation Pourbaix Diagram



Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *Electro. Chem. Sci. Adv.* **2021**, 2100142.

Acknowledgements

Dr. Rachelle M. Choueiri

Stephen W. Tatarchuk

Prof. Anna Klinkova

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Fonds Nouvelles frontières en recherche

NSERC
CRSNG

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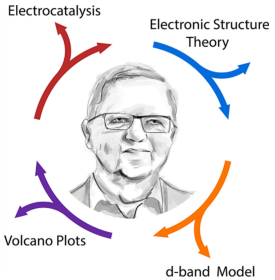
Acknowledgements

I am grateful to Kathrine Nielsen and Thomas Bligaard
for inviting me to this Symposium.



Medford, A. J.; Moses, P. G.; Jacobsen, K. W.; Peterson, A. A. *ACS Catal.* **2022**, *12*, 9679–9689.

Happy 70th Birthday, Jens!