Ab Initio Computational Modelling of Electrochemical Reactions

ETC-ECS Student Chapter Speaker Series

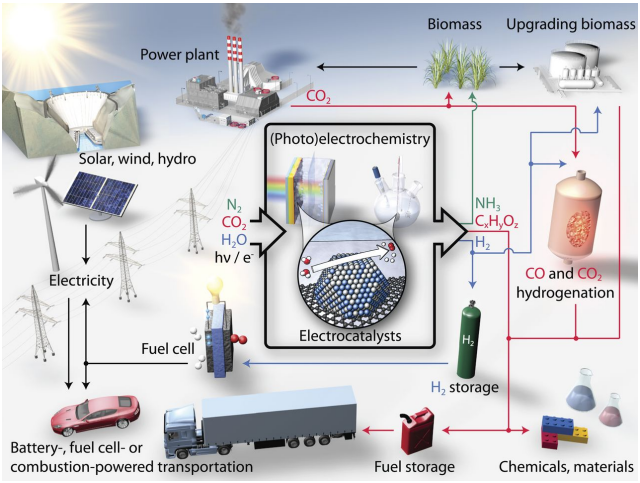
Leanne D. Chen

June 18th, 2021

University of Guelph

ELECTROCHEMICAL TECHNOLOGY CENTRE
DEPARTMENT OF CHEMISTRY

The Energy Transformation Challenge



Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Jaramillo, T. F. *Science* **2017**, *355*, eaad4998.

mechanistic understanding

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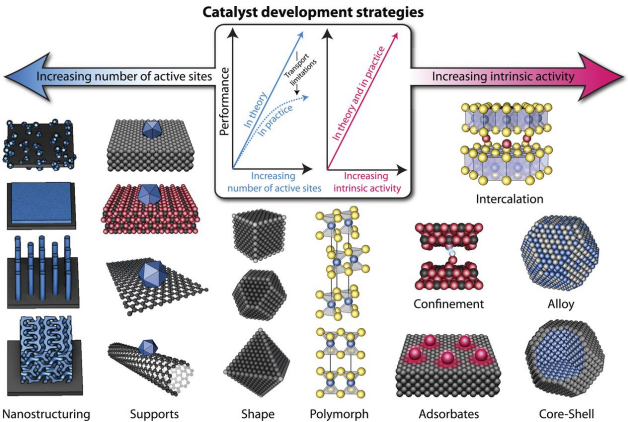
stable, active, and selective electrocatalysts

Improving Electrocatalytic Activity



Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Jaramillo, T. F. *Science* **2017**, *355*, eaad4998.

mechanistic understanding

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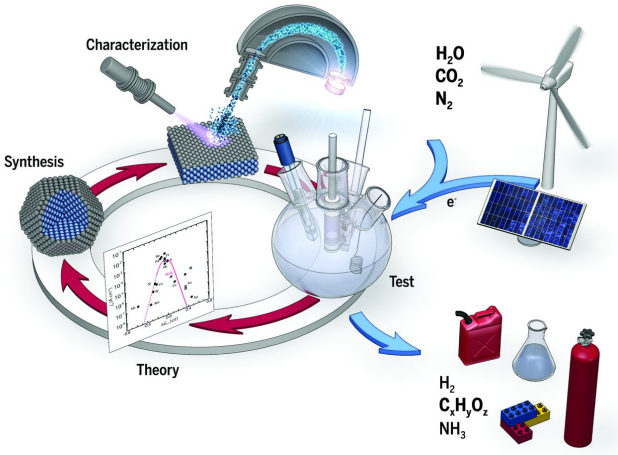
stable, active, and selective electrocatalysts

Theory + Experiment



mechanistic understanding

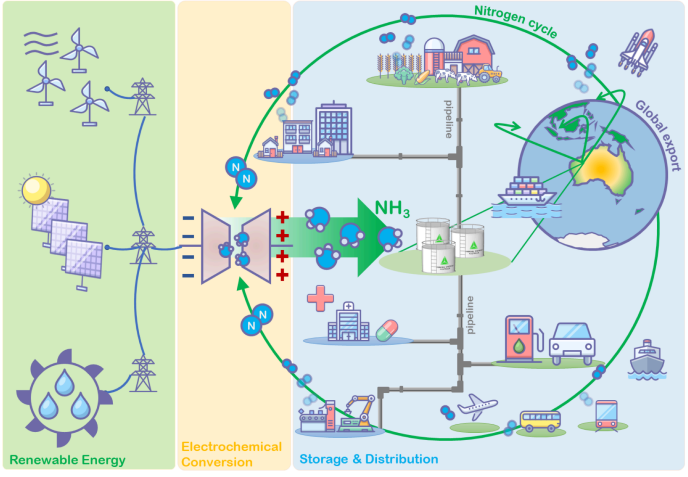
↓

stable, active, and selective electrocatalysts

Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Jaramillo, T. F. *Science* **2017**, *355*, eaad4998.

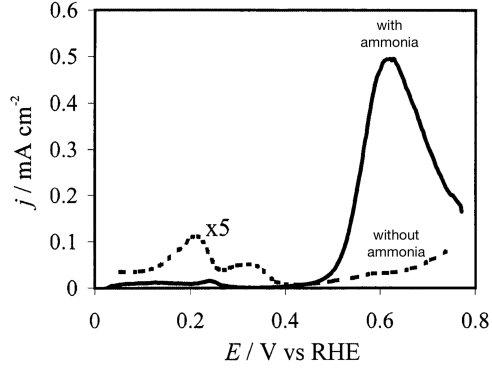
Ni-based Materials for Electrochemical Ammonia Oxidation

The Ammonia Economy

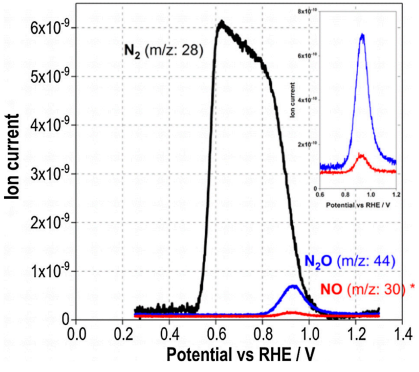


MacFarlane, D. R.; Cherepanov, P. V.; Choi, J.; Suryanto, B. H. R.; Hodgetts, R. Y.; Bakker, J. M.; Ferrero Vallana, F. M.; Simonov, A. N. *Joule* **2020**, *4*, 1186–1205.

NH_3 Oxidation on Pt

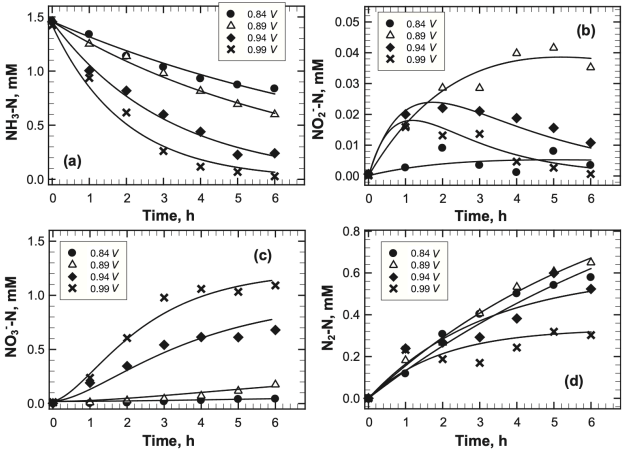


de Vooys, A. C. A.; Koper, M. T. M.; van Santen, R. A.; van Veen, J. A. R. *Electroanal. Chem.* **2001**, *506*, 127–137.



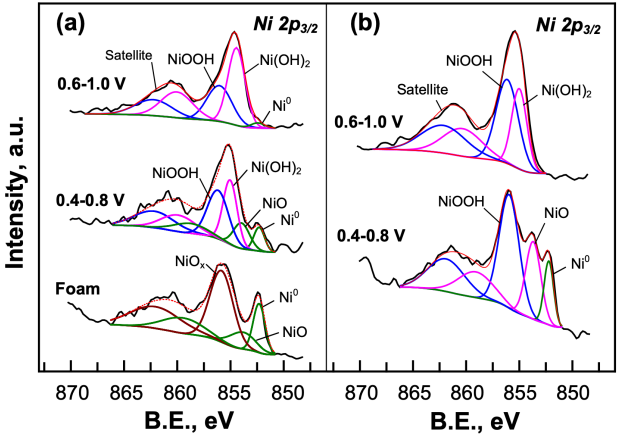
Katsounaros, I.; Figueiredo, M. C.; Calle-Vallejo, F.; Li, H.; Gewirth, A. A.; Marković, N. M.; Koper, M. T. M. *J. Catal.* **2018**, *359*, 82–91.

NH_3 Oxidation on NiO_xH_y



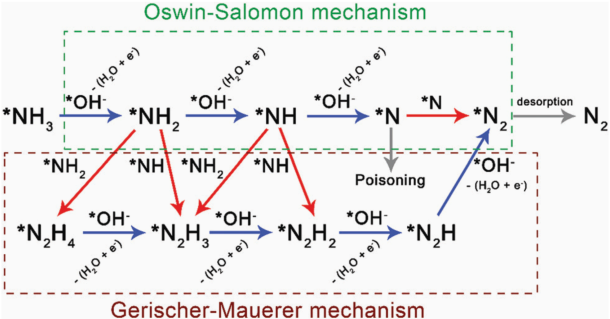
Shih, Y.-J.; Huang, Y.-H.; Huang, C. P. *Electrochim. Acta.* **2018**, *263*, 261–271.

NH_3 Oxidation on NiO_xH_y



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).

Surface Processes

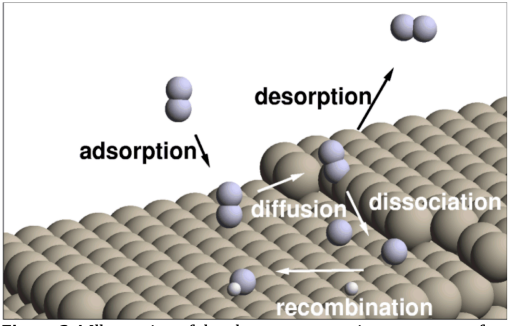
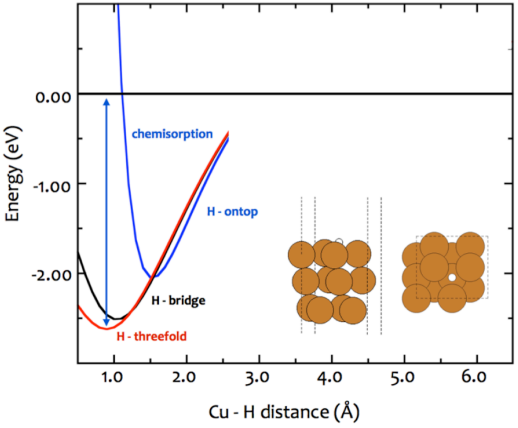


Figure 2.4 Illustration of the elementary reaction steps on surfaces.



Nørskov, J. K.; Studt, F.; Abild-Pedersen, F.; Bligaard, T. John Wiley & Sons, Inc: Hoboken, NJ, USA, 2014.

The Computational Hydrogen Electrode (CHE)

Origin of the overpotential for oxygen reduction at a fuel-cell cathode

Authors	Jens Kehlet Nørskov, Jan Rossmeisl, Ashildur Logadottir, LRKJ Lindqvist, John R Kitchin, Thomas Bligaard, Hannes Jonsson
Publication date	2004/11/18
Journal	The Journal of Physical Chemistry B
Volume	108
Issue	46
Pages	17886-17892
Publisher	American Chemical Society
Description	We present a method for calculating the stability of reaction intermediates of electrochemical processes on the basis of electronic structure calculations. We used that method in combination with detailed density functional calculations to develop a detailed description of the free-energy landscape of the electrochemical oxygen reduction reaction over Pt(111) as a function of applied bias. This allowed us to identify the origin of the overpotential found for this reaction. Adsorbed oxygen and hydroxyl are found to be very stable intermediates at potentials close to equilibrium, and the calculated rate constant for the activated proton/electron transfer to adsorbed oxygen or hydroxyl can account quantitatively for the observed kinetics. On the basis of a database of calculated oxygen and hydroxyl adsorption energies, the trends in the oxygen reduction rate for a large number of different transition and noble metals can be …
Total citations	Cited by 5667

The Computational Hydrogen Electrode (CHE)

Our reference is the half-reaction

$$H^+(aq) + e^- \rightleftharpoons \frac{1}{2} H_2(g) \tag{1}$$

This reaction is defined to be at equilibrium at $U = 0$ V, pH $= 0$, and $p_{H_2} = 101325$ Pa. Then we can equate the chemical potentials of the proton-electron pair with half that of the gas-phase H_2 molecule

$$\mu_{H^+(aq)} + \mu_{e^-} = \frac{1}{2}\mu_{H_2(g)} \tag{2}$$

Additional terms are added to include the effects of pH and potential shifts

$$\mu_{H^+(aq)}([H^+]) + \mu_{e^-}(U) = \frac{1}{2}\mu_{H_2(g)} + RT \ln \left(\frac{\sqrt{p_{H_2}}}{[H^+]} \right) - eU \tag{3}$$

Nørskov, J.K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H. *J. Phys. Chem. B* **2004**, *108*, 17886–17892.

Applying the CHE in Alkaline Conditions

$$\mathrm{H_2O(l)} + \mathrm{e^-} \rightleftharpoons \frac{1}{2}\,\mathrm{H_2(g)} + \mathrm{OH^-(aq)}, \quad U^{\ominus} = -0.83\ \mathrm{V\ versus\ SHE,\ pH = 14} \tag{4}$$

$$\mu_{\mathrm{OH^-(aq)}} - \mu_{\mathrm{e^-}} = \mu_{\mathrm{H_2O(l)}} - \frac{1}{2}\mu_{\mathrm{H_2(g)}} + RT\ln\left(\frac{\sqrt{p_{\mathrm{H_2}}}\left[\mathrm{OH^-}\right]}{a_{\mathrm{H_2O(l)}}}\right) - (0.83 + eU) \tag{5}$$

To calculate the energy change of an adsorption step

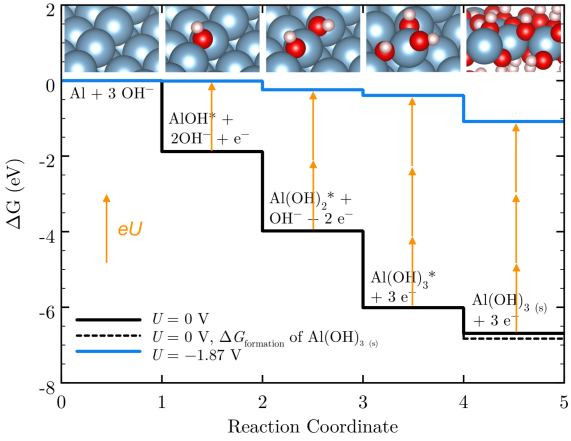
$$\mathrm{Al} + \mathrm{OH^-(aq)} \rightarrow \mathrm{AlOH}* + \mathrm{e^-} \tag{6}$$

We have

$$\Delta G = G_{\mathrm{AlOH}*} - G_{\mathrm{Al}} - \left[\mu_{\mathrm{H_2O(l)}} - \frac{1}{2}\mu_{\mathrm{H_2(g)}} + RT\ln\left(\frac{\sqrt{p_{\mathrm{H_2}}}\left[\mathrm{OH^-}\right]}{a_{\mathrm{H_2O(l)}}}\right) - (0.83 + eU)\right] \tag{7}$$

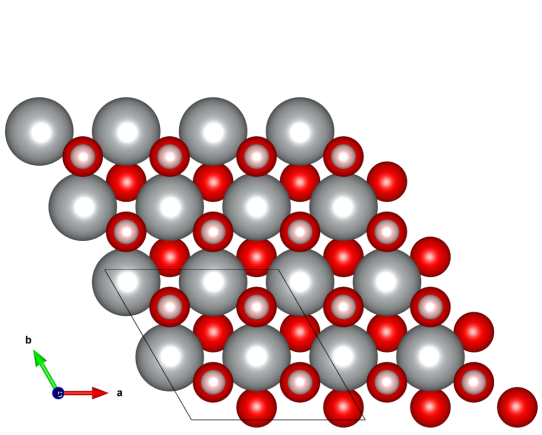
Chen, L. D.; Nørskov, J. K.; Luntz, A. C. *J. Phys. Chem. Lett.* **2014**, *119*, 19660–19667.

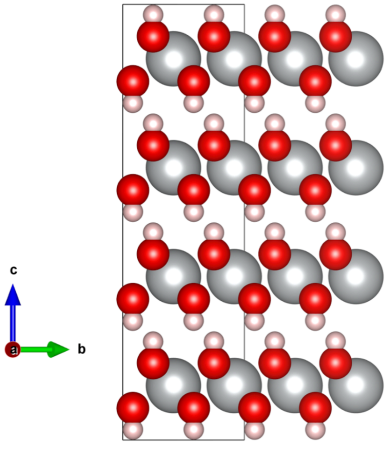
Applying the CHE in Alkaline Conditions



Chen, L. D.; Nørskov, J. K.; Luntz, A. C. *J. Phys. Chem. Lett.* **2014**, *119*, 19660–19667.

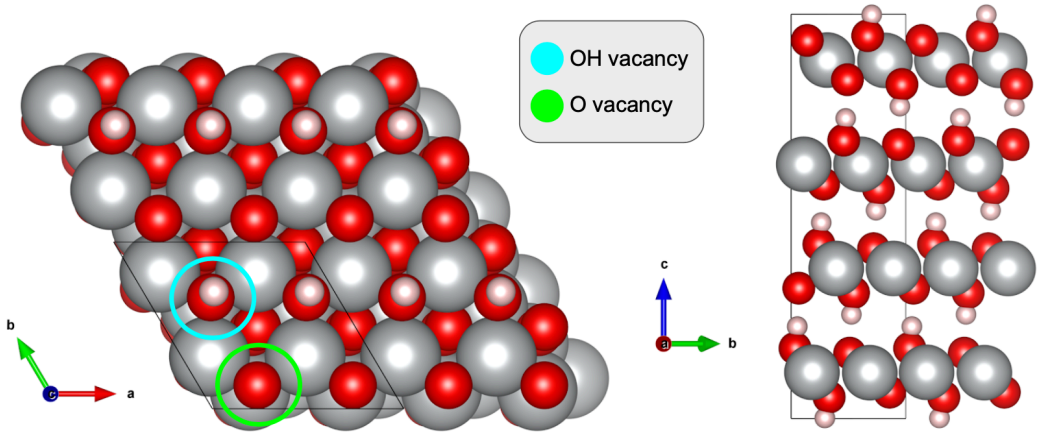
Structure of β-Ni(OH)$_2$





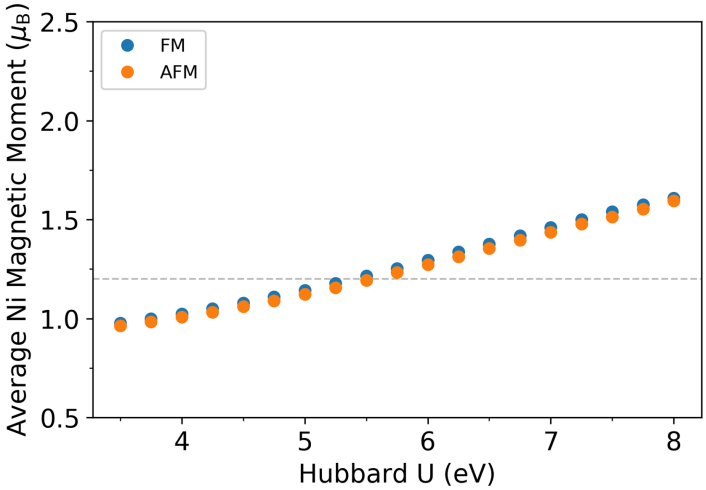
Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *In Prep.*

Structure of β-NiOOH



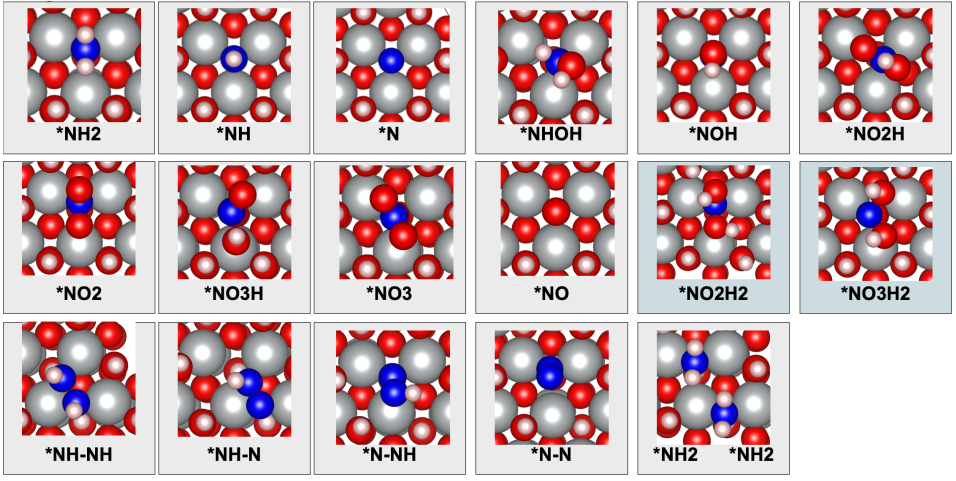
Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *In Prep.*

Hubbard *U* Determination



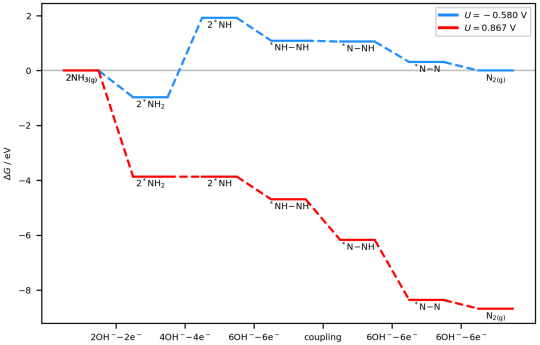
Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *In Prep.*

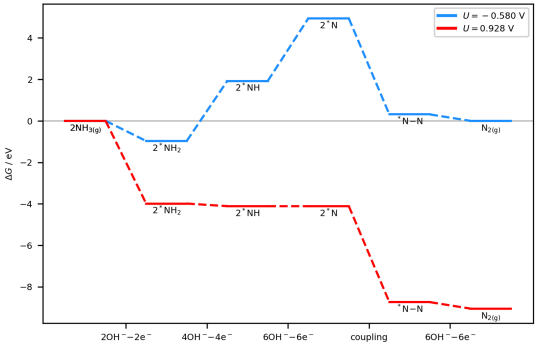
Reaction Intermediates



Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *In Prep.*

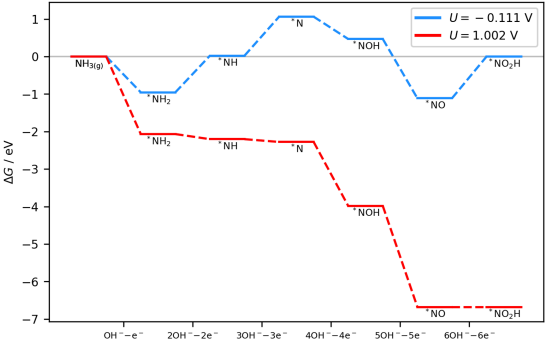
Formation of N_2 on β-$Ni(OH)_2$

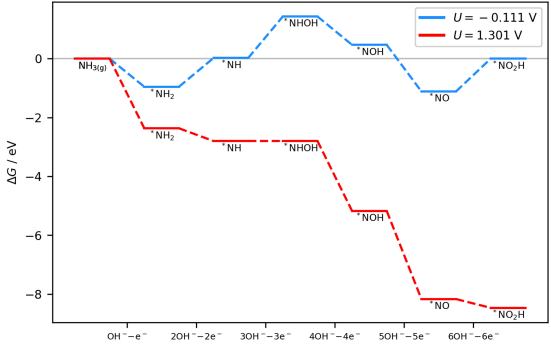




Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *In Prep.*

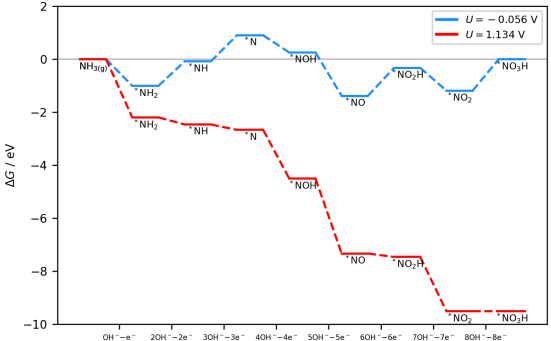
Formation of NO_2^- on β-$Ni(OH)_2$

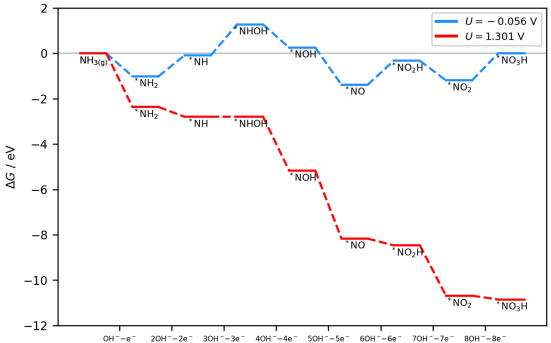




Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *In Prep.*

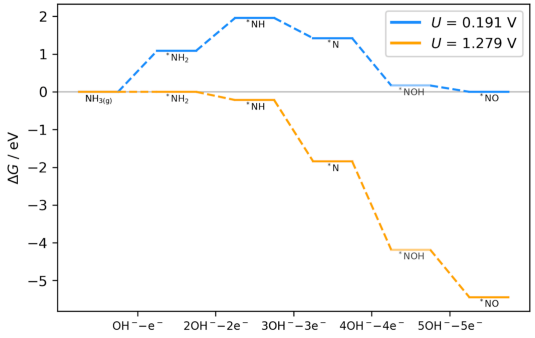
Formation of NO_3^- on β-$Ni(OH)_2$

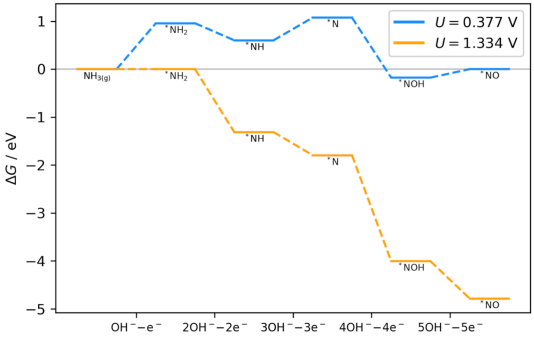




Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *In Prep.*

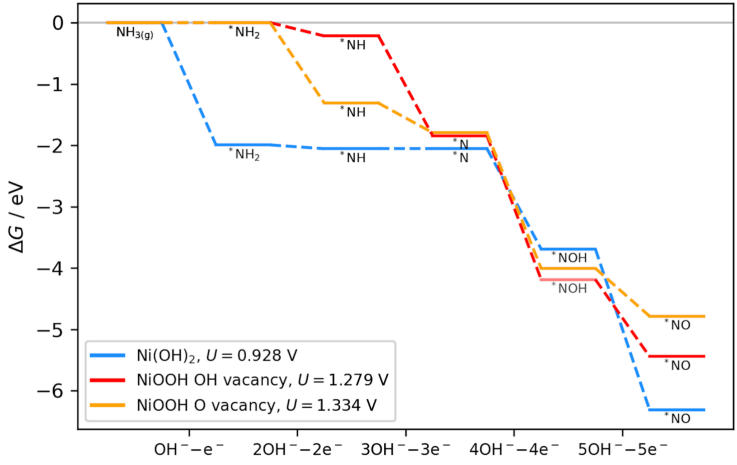
Formation of NO on β-NiOOH





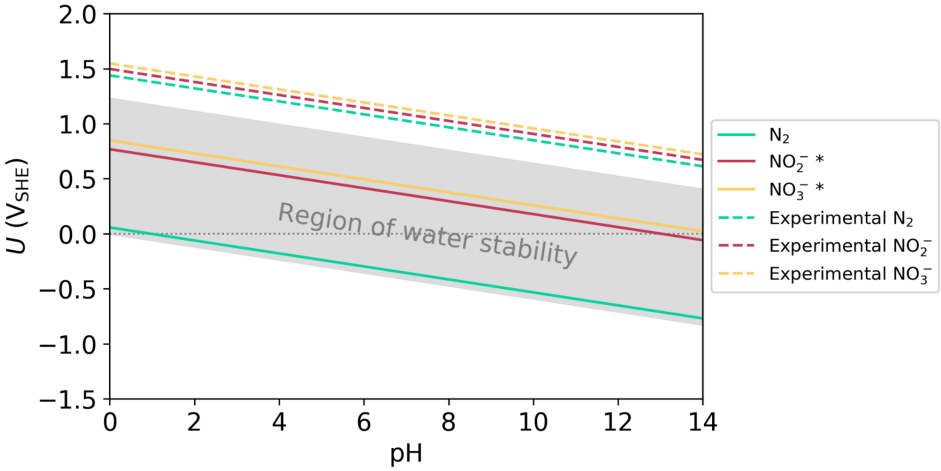
Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *In Prep.*

Comparison of Limiting Potentials for β-Ni(OH)$_2$ and β-NiOOH



Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *In Prep.*

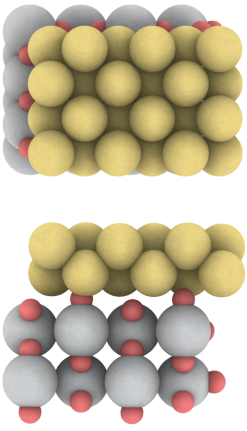
Ammonia Oxidation Pourbaix Diagram

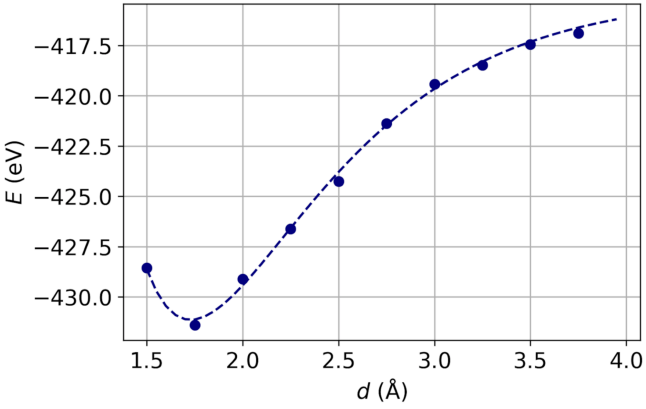


Choueiri, R. M.; Tatarchuk, S. W.; Klinkova, A.; Chen, L. D. *In Prep.*

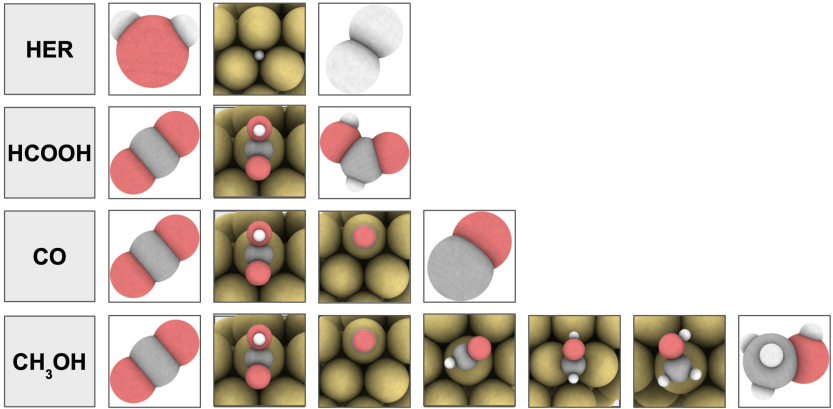
Electrochemical Reduction of Carbon Dioxide on TiO_2@Au Nanoparticles

Computational Model for TiO_2@Au

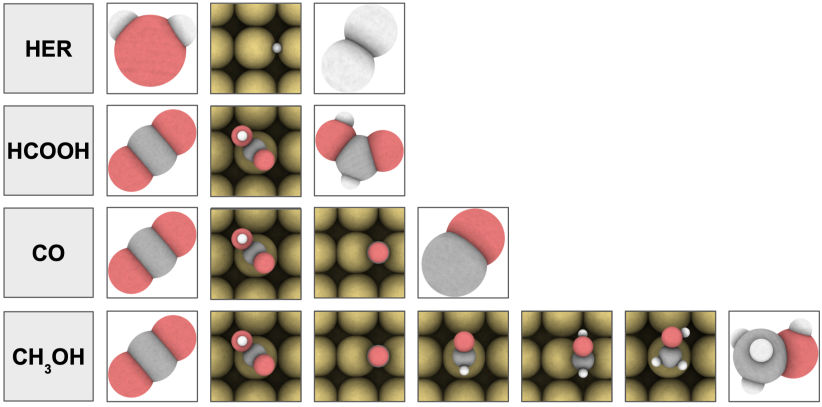




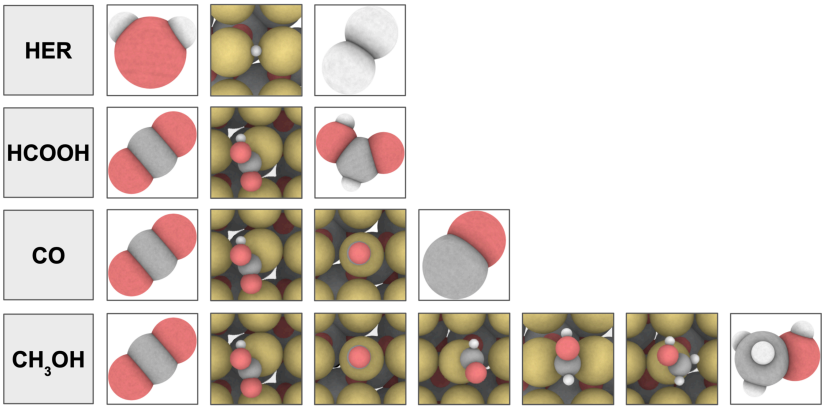
HER and CO_2RR Pathways on Au(111)



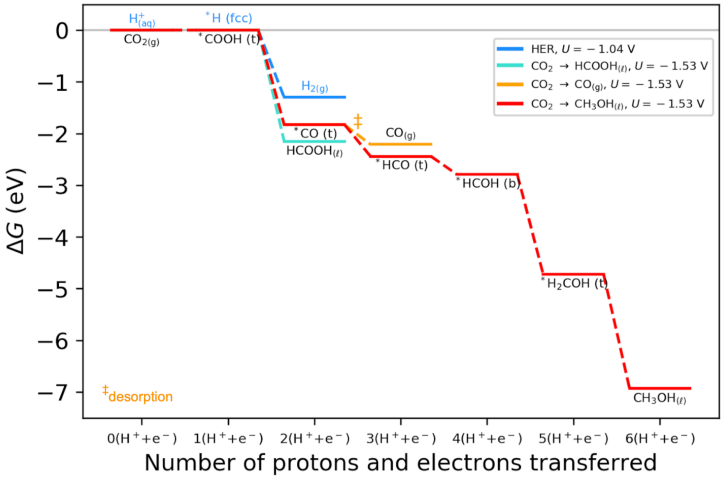
HER and CO_2RR Pathways on Au(100)



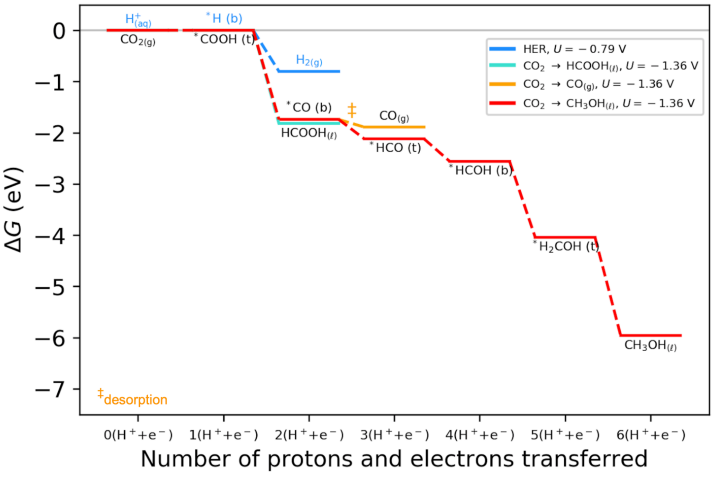
HER and CO_2RR Pathways on TiO_2(110)@Au(100)



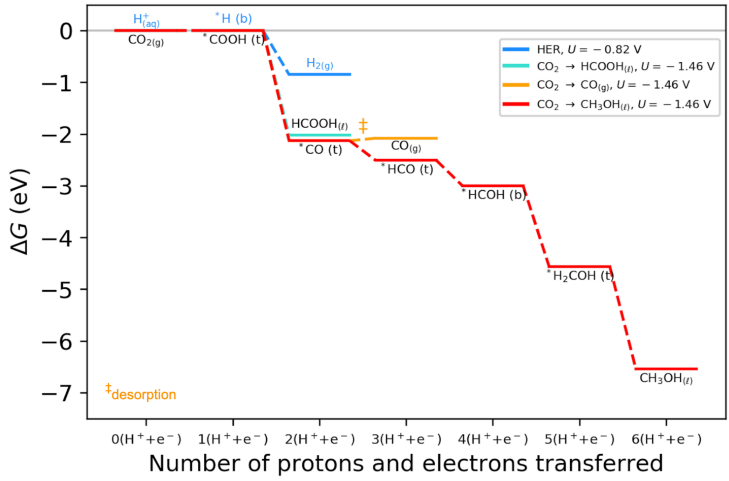
Free Energy Diagram on Au(111)



Free Energy Diagram on Au(100)



Free Energy Diagram on TiO_2(110)@Au(100)



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- Scott Prins
- Prof. Anna Klinkova
- Prof. Aicheng Chen

New Frontiers in Research Fund
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Acknowledgements

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for inviting me to be a part of the ETC-ECS Student Chapter Speaker Series!