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Dear Editors of *Communications Chemistry*,

We are submitting an invited research article titled “Potential Dependence of Nitrate Adsorption and Dissociation across Metals and Dilute Alloys: a Grand Canonical Study” for your consideration. We were invited to contribute an article to a Collection on *Electroreduction of activated nitrogen compounds* by Guest Editor Dr. Kelsey Stoerzinger.

In our article, we computationally study the potential dependence of nitrate (NO3-) adsorption and dissociation across pure metals and single atom alloys (SAAs) using Grand Canonical Density Functional Theory (GC-DFT). The electrocatalytic reduction of nitrate (ENR) is being seriously considered by the scientific community as a sustainable approach to produce ammonia or other value-added nitrogen products while remediating nitrate pollution. However, the impact of the applied electrochemical potential on key reaction steps within nitrate reduction is not well understood, as well as the influence of dilute alloying on the potential dependence, which limits mechanistic understanding and rational catalyst design. We use both explicit GC-DFT and analytical GC-DFT methods to: (1) evaluate the thermodynamic tendency of SAA dopant atoms to segregate or aggregate under applied potentials in the presence of nitrate and hydrogen, (2) compute the electrosorption valencies for nitrate adsorption and symmetry factors for nitrate dissociation across pure metals and stable/meta-stable SAAs, and (3) demonstrate the sensitivity of predictions to properties of the electrochemical double layer. Our main findings are summarized below.

1. Using explicit GC-DFT to account for structural changes under applied potentials, we find that Pd1Cu(111) is stable against surface segregation and aggregation across many ENR relevant conditions while (111) facets of Ni1Cu, Ru1Cu, and Rh1Cu maintain positive or near-zero segregation energies with low to moderate aggregation energies in the presence of adsorbed hydrogen and nitrate.
2. Using analytical GC-DFT (which we found gives similar results as explicit GC-DFT), we demonstrate that the change in the surface normal moment dictates the potential dependence for nitrate adsorption and dissociation for both pure metals and SAAs. The electrosorption valencies for nitrate adsorption across catalysts range from 0.60 eV/V to 0.80 eV/V, which correlate with the extent of charge transfer to the surface for both pure metals and SAAs. In contrast, the computed symmetry factors for direct nitrate dissociation to nitrite indicate a small potential dependence for this reaction step across all catalysts (0.04 eV/V to 0.20 eV/V), with no clear relation to charge transfer to or from the surface. These results greatly differ from the commonly used computational hydrogen electrode model.
3. For Ni1Cu, an experimentally studied SAA for nitrate reduction, analytical GC-DFT predicts potential-dependent adsorption and activation energies that can differ significantly (i.e., between 3.0 kJ/mol and 60 kJ/mol) from approximations by conventional methods that neglect the effects of the electrochemical double layer. Furthermore, we demonstrate these errors in calculated reaction energetics vary drastically across different catalysts and with the assumed electrochemical double layer properties within GC-DFT.

Ultimately, this article advances knowledge about the potential dependence of key reaction steps within the nitrate reduction reaction mechanisms on metals and SAAs. We believe this article meets the high standards of *Communications Chemistry* and would be of interest to researchers studying NOx- electrocatalysis and the wider electrochemistry community. This manuscript has not been submitted elsewhere or previously considered for publication. Suggested reviewers are listed below.

Thank you for your time and consideration.

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| **A black background with a black square  AI-generated content may be incorrect.**  **Dean M. Sweeney**  Graduate Student  University of Michigan Ann Arbor | **Bolton Tran, Ph.D.**  Postdoctoral Researcher  University of Michigan Ann Arbor | **Bryan R. Goldsmith, Ph.D.**  Dow Corning Assistant Professor of Chemical Engineering  University of Michigan Ann Arbor |

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