Elucidating Ammonia Electrooxidation Reaction Mechanisms on β-Ni(OH)₂/NiOOH Surfaces with Density Functional Theory

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The ammonia electrooxidation reaction (AOR) is a promising method for the treatment and upcycling of excess ammonia in wastewater effluent as well as a key step in facilitating the ammonia economy--a proposal to use ammonia as a primary fuel in a closed loop fashion. β-Ni(OH)₂/NiOOH is an attractive AOR electrocatalyst material due to its lower cost and higher resistance to poisoning relative to traditional Pt-based AOR catalysts. Currently, the β-Ni(OH)₂/NiOOH system suffers from high overpotentials which are ca. 1 V greater than the theoretical potential for nitrogen gas production. To date, while the mechanism of AOR on Pt surfaces has been studied in depth, the mechanism of AOR on β-Ni(OH)₂/NiOOH has not been elucidated. In this work, we compare the Gibbs free energy of AOR intermediates for pathways that produce nitrogen gas, aqueous nitrite, and nitrate from ammonia on the (0001) facet of both β-Ni(OH)₂ and NiOOH surfaces and compute limiting potentials using density functional theory (DFT) and the computational hydrogen electrode. Due to the unresolved nature of the β-NiOOH structure, we include a systematic comparison of the various structures proposed in the literature (both theoretical and experimental) as well as a discussion of the origin of various Hubbard U parameters employed in DFT calculation. We also compute and compare the Hubbard U parameter determined by linear response theory and by matching computed β-NiOOH cell interlayer spacings with experiment. Following this, we computed the energies of adsorbate-surface interactions to uncover potential electrocatalyst poisons, preferred substrate and intermediate adsorption sites, and likely AOR pathways including the lowest energy NH_x-NH_y coupling pathway on both surfaces. All calculations were corrected for experimental pH conditions and computed potentials were compared to existing electrochemical data in the literature. In sum, the goal of this work is to provide a departure point for further modification and understanding of the β-Ni(OH)₂/NiOOH system and to set the stage for future computational screening of Ni-based AOR catalysts to improve energy efficiency and product selectivity.