

Moving Protons with Pendant Amines in Niobium-Based Electrocatalysts

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Abstract: The controlled mobility of protons is a fundamental step in a series of chemical and biological reduction-oxidation processes, such as the reduction of dioxygen to water and the production/oxidation of hydrogen [1,2]. The tailoring of molecular electrocatalysts that effectively forms or cleaves the H-H bond is, therefore, extremely useful for the energy storage problem [3]. Such catalysts, responsible for the electrochemical transformation of abundant substrates into fuels, should be efficient and based on low-cost and abundant metals. In this perspective, Brazil has the largest Niobium (Nb) reserves in the world (98.53%) and exportation as ferroniobium, a type of iron-Nb alloy, is the main commercial destination of the metal [4]. The goal of this work is to aggregate economic and technological value to Nb by developing coordination compounds based on the metal that present electrocatalytic activity for energy-relevant conversions. The intramolecular proton transfer between Nb and positioned pendant amines for the hydrogen oxidation electrocatalyst $[\text{Nb}_2(\text{P}^{\text{Cy}}_2\text{N}^{\text{Bn}}_2\text{H})_2]^{2+}$ ($\text{P}^{\text{Cy}}_2\text{N}^{\text{Bn}}_2 = 1,5\text{-dibenzyl-3,7-dicyclohexyl-1,5-diaza-3,7-diphosphocyclooctane}$, Figure 1) is described herein by Density Functional Theory (DFT) calculations at the B3P86/{Nb(SDD);P,N,C,H(6-31G**)} level. This ligand was successfully applied in early studies for the generation of Ni-based electrocatalysts, in which both experimental and computational results pointed to a metal-mediated intramolecular proton transfer between the nitrogen atoms, and chair-to-boat isomerizations as rate-limiting steps [5]. Important details of the geometrical and energetic properties of Nb-based electrocatalysts are discussed. The authors hope that this study will provide key aspects for the production of a new generation of molecular electrocatalysts based on Niobium.

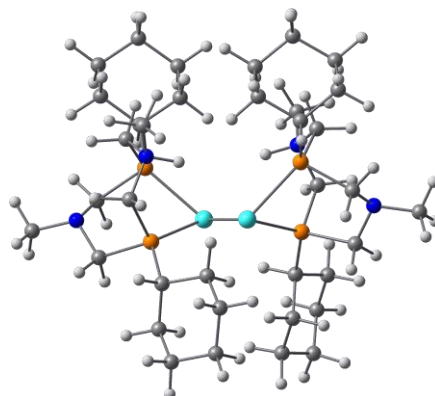


Figure 1. The hydrogen oxidation electrocatalyst $[\text{Nb}_2(\text{P}^{\text{Cy}}_2\text{N}^{\text{Bn}}_2\text{H})_2]^{2+}$.



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