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A simple method for the preparation of bio-inspired nickel bisdiphosphine hydrogen-evolving catalysts



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ABSTRACT

We herein report on a novel, simple and straightforward method for the preparation of nickel bisdiphosphine hydrogen-evolving catalysts, so-called DuBois catalysts, from commercially available nickel hexaaqua salts. This method yields coordination complexes with the same physical characteristics as previously described for compounds prepared from the $[\text{Ni}(\text{CH}_3\text{CN})_6]^{2+}$ precursor. However, if hexaaquanickel(II) chloride is used as a precursor, a different nickel bisdiphosphine complex is formed, which incorporates chloride as an axial ligand. This complex displays a significantly different electrochemical behavior and a diminished activity for proton reduction as compared to classic DuBois catalysts.

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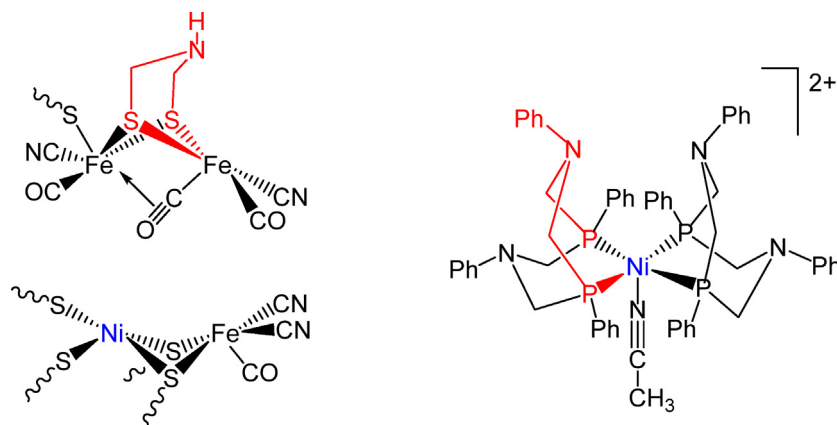
1. Introduction

Hydrogen production, through the reduction of water in electrolyzers, is currently one of the most convenient ways to store energy durably, provided that electrical energy is initially obtained from renewable resources. While electrolysis is a mature and robust technology, the most promising devices, based on proton exchange membranes, rely on the use of platinum as an electrocatalyst to accelerate both hydrogen evolution and water oxidation reactions. This rare and expensive metal is not itself a renewable resource, so the viability of a hydrogen economy depends on the design of new efficient and robust electrocatalytic materials based on Earth-abundant

elements. A competitive alternative to platinum could be found in living micro-organisms that metabolize hydrogen using hydrogenases [1,2]. Catalysis in hydrogenases requires only base-metal centers (nickel and iron), and the structures of their active sites have inspired the design of new synthetic catalysts based on these metals [3–8], cobalt [8,9], or other Earth-abundant elements such as molybdenum [10] and manganese [11]. Probably one of the most successful examples of such a bio-inspired approach is the series of nickel bisdiphosphine complexes designed by D. L. DuBois (Scheme 1) [12,13]. While structurally dissimilar to hydrogenase active sites (Scheme 1), these compounds combine features of both $[\text{NiFe}]$ - and $[\text{FeFe}]$ -hydrogenases, borrowing the Ni ion from the former, and from the latter the pendant amine groups [14,15], which act as a proton relay in the enzymatic mechanism. Depending on the nature of the substituents on the N and P atoms, these compounds have been shown

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Scheme 1. (Color online.) Representation of the $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})]^{2+}$ cation (right) and of the active sites of the $[\text{FeFe}]$ -hydrogenase in the reduced H_{red} state (top left), and the $[\text{NiFe}]$ -hydrogenase in the Ni-SI state (bottom left).

to display remarkable catalytic properties for hydrogen evolution, and currently stand as the only series capable of catalytic hydrogen oxidation, with some compounds being able to achieve bidirectional catalysis [16,17]. Immobilization of such synthetic catalysts on multiwall carbon nanotubes (CNTs), either covalently or through π - π stacking interactions, has yielded catalytic nanomaterials that when interfaced with a Nafion membrane show bidirectional and reversible catalytic activity for hydrogen evolution and oxidation at the thermodynamic equilibrium, prolonged stability under turnover conditions, and resistance to CO poisoning [2,18,19]. However, the reported preparation of such nickel bisdiphosphine compounds requires the use of anhydrous nickel salts in the form of the hexakisacetonitrilenickel(II) complex, which must be synthesized by the oxidation of metallic nickel by nitrosonium cations in acetonitrile. We report herein that the same nickel bisdiphosphine complexes can be prepared starting from hydrated nickel salts. Additionally, in the course of this study, we identified that chloride anions can bind to the nickel center in nickel bisdiphosphine complexes, which significantly affects their electrochemical behavior and strongly diminishes their catalytic activity for hydrogen evolution.

2. Results and discussion

The reaction of $[\text{Ni}(\text{H}_2\text{O})_6](\text{BF}_4)_2$ or $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ with two equivalents of the $\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2$ diphosphine ligand (Scheme 1) in acetonitrile yields the corresponding nickel complexes $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{BF}_4)_2$ (**1**) and $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2(\text{CH}_3\text{CN})](\text{ClO}_4)_2$ (**2**) in good yields. These complexes show ^1H and ^{31}P NMR spectra similar to those of the complex synthesized from the hexakisacetonitrilenickel(II) precursor as prepared in our laboratory and previously reported by DuBois and coworkers [12]. The cyclic voltammograms of complexes **1** and **2** (Fig. 1), recorded in acetonitrile at a glassy carbon electrode, both display a reversible reduction at -0.84 V vs $\text{Fc}^{+/0}$ (peak-to-peak separation of 70 mV), followed by a quasi-reversible reduction at -1.02 V vs $\text{Fc}^{+/0}$ (which becomes irreversible at scan rates below 100 mV s^{-1}). These data compare well

to the one-electron reductions at -0.84 V and -1.02 V vs $\text{Fc}^{+/0}$ reported by DuBois [12] and also to the values of -0.82 V and -1.03 V vs $\text{Fc}^{+/0}$ obtained from a sample prepared in our laboratory (Fig. 1). The same procedure also allowed the preparation of the $[\text{Ni}(\text{P}_2^{\text{Ph}}\text{N}_2^{\text{Bz}})_2](\text{ClO}_4)_2$ compound, again with similar characteristics as those previously reported for a complex prepared from $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$.

The addition of increasing amounts of the acid $[\text{DMFH}]\text{OTf}:\text{DMF}$ results in the appearance of a catalytic wave with half-wave potential of -0.92 V and -0.89 V vs $\text{Fc}^{+/0}$ for compounds **1** and **2**, respectively. These values compare well with the half-wave potential of -0.86 V vs $\text{Fc}^{+/0}$ as reported by DuBois [20,21]. An i_c/i_p plot for **1** (Fig. 2, inset) shows the catalytic current upon addition of acid, normalized to the current of the first reduction peak in the absence of acid, as a function of acid concentration [22]. Overlaying this plot with that obtained for the complex prepared from the hexakisacetonitrilenickel(II) precursor shows identical catalytic activities.

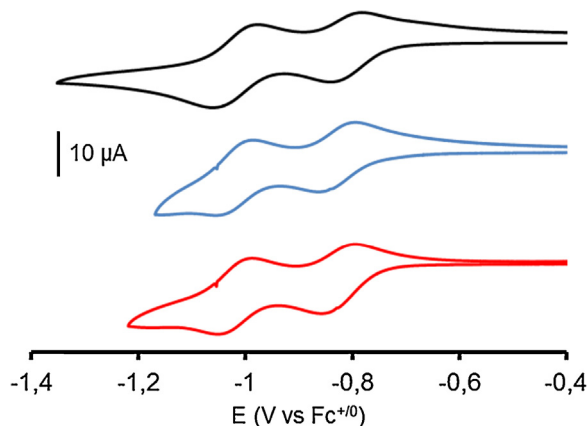


Fig. 1. (Color online.) Cyclic voltammograms of compounds **1** (blue trace), **2** (red trace) and $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)_2](\text{BF}_4)_2$ (black trace) prepared from $[\text{Ni}(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$ ($1\text{ mmol}\cdot\text{L}^{-1}$, GC working electrode, $100\text{ mV}\cdot\text{s}^{-1}$, $0.1\text{ mol}\cdot\text{L}^{-1}$ $n\text{-Bu}_4\text{NBF}_4$ in MeCN, potentials are quoted versus the $\text{Fc}^{+/0}$ couple).

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