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Application of Gold Electrodes for the Study of Nickel Based Homogeneous Catalysts for Hydrogen Oxidation

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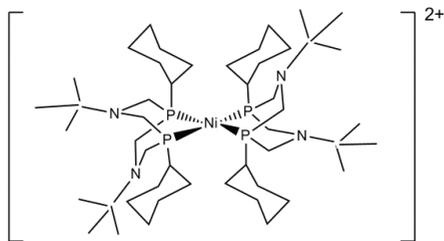
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1. Introduction

The study of homogeneous electrocatalysts for the hydrogen evolution and oxidation reactions contributes to our understanding of hydrogenase enzymes and provides a foundation for the rational development of synthetic catalysts for use in energy technologies. [1-7] Recently, turnover frequencies as high as 50 s^{-1} for hydrogen oxidation [4] and above 10^5 s^{-1} for hydrogen evolution [7] have been observed for functional hydrogenase mimics in acetonitrile solution, with these reversible nernstian catalysts generally operating at proton-coupled mechanism and larger overpotentials than the enzymes themselves. Glassy carbon electrodes are typically used as working electrodes in these studies, as this material is inert for hydrogen oxidation and reduction thus minimizing background currents corresponding to electrode-catalyzed reactions.

[1, 3, 4] In this contribution, we will examine the role of the electrode material in studies of homogeneously catalyzed hydrogen oxidation and demonstrate the practicality of gold electrodes as an alternative to glassy carbon.

Gold is active for hydrogen evolution reaction in organic solvents at potentials near that of platinum. [8] However, gold like carbon does not catalyze hydrogen oxidation. [8] The real advantage of gold is that it can be used in electrode configurations that are difficult to achieve with carbon, including but not limited to mesh electrodes for spectroelectrochemical cells, [9, 10] interdigitated array electrodes [11] and scanning electrochemical microscope probe tips [12, 13] where gold electrodes are easy to fabricate. [14-17] *Scheme 1* shows the structure of the nickel bis(diphosphine) hydrogen oxidation catalyst $Ni(P^{Cy}_2N^{t-Bu}_2)_2^{2+}$.



Scheme 1: Schematic presentation of $\text{Ni}(\text{PCy}_2\text{N}^{\text{t-Bu}})_2^{2+}$

2. Experimental

Cyclic voltammograms were recorded using an IVIUM compact bipotentiostat (Eindhoven, the Netherlands). A sealed three-electrode cell (ACE Glass, Vineland, NJ) was loaded and assembled in an inert-atmosphere glovebox for all experiments, with a bare silver wire acting as a quasi-reference electrode and a platinum wire or a glassy carbon rod (Alfa Aesar, Ward Hill, MA) as a counter electrode. All potentials for electrochemical experiments were calibrated using the measured $E_{1/2}$ value for the ferrocene/ferrocenium redox couple ($\text{Cp}_2\text{Fe}^{+/0}$, 0 V). Working electrodes (CH instruments, Austin, TX) were gold, glassy carbon (0.5 mm radius) and 1 mm platinum, and were polished with 0.3 μm alumina and thoroughly dried in the flow of nitrogen prior transferring to the glovebox. Benzonitrile was used as a solvent in the catalytic process and for the reaction at platinum electrodes. Hydrogen gas (UHP, Praxair Inc., Danbury, CT) was purified by passage through an oxygen/moisture/hydrocarbon trap (Restek, Bellefonte, PA). Electrochemical grade tetra-n-butylammonium hexafluorophosphate (TBAPF_6), triethylamine (TEA, 99 %) and benzonitrile (99.8 %) were obtained from Sigma-Aldrich (Milwaukee, WI) and used as received.

3. Results and discussion

Figure 1a shows cyclic voltammograms for $\text{Ni}(\text{PCy}_2\text{N}^{\text{t-Bu}})_2^{2+}$ in benzonitrile exhibiting two

reversible one-electron waves assigned to the $\text{Ni}(\text{II}/\text{I})$ and $\text{Ni}(\text{I}/0)$ redox couples (-0.8 V and -1.45 V vs $\text{Cp}_2\text{Fe}^{+/0}$, respectively) [4] at gold electrode. Cyclic voltammograms, with added triethylamine (TEA) and under 1 atm hydrogen, using both glassy carbon and gold electrodes of the same nominal size are shown in Figure 1b. These voltammograms are essentially identical, indicating the suitability of either electrode material in the study of homogeneous catalysis of hydrogen oxidation under these conditions. The increase of current from 0.2 μA to 16 μA because of catalytic process is clearly visible. Turnover frequencies of 48-56 s^{-1} under 1 atm. hydrogen are calculated and are in the same range as previously reported values. [4] Presence of first order kinetics for nickel catalyst concentration, independence on the base concentration in case of excess of it and according to that an ECcat. (EC') mechanism was assumed in all calculations: [1]

- $i_c/i_p = (n/0.4463) * (\text{RT}k_{\text{obs}}/Fv)^{1/2}$
where k_{obs} is turnover frequency, i_c is a catalytic current and i_p a peak current for reaction in the absence of catalyst and v scan rate of the reaction.
- $\text{Ni}(\text{PCy}_2\text{N}^{\text{t-Bu}})_2^{2+} + \text{H}_2 = \text{Ni}(\text{PCy}_2\text{N}^{\text{t-BuH}})_2$
- $\text{Ni}(\text{PCy}_2\text{N}^{\text{t-BuH}})_2 = \text{Ni}(\text{PCy}_2\text{N}^{\text{t-BuH}})_2^{2+} + 2e$
- $\text{Ni}(\text{PCy}_2\text{N}^{\text{t-BuH}})_2^{2+} + \text{TEA} = \text{Ni}(\text{PCy}_2\text{N}^{\text{t-BuH}})_2 +$
(decomposition products)

The obtained results are different compared with platinum electrodes, where heterogeneous oxidation waves for hydrogen oxidation appear at more negative potentials compared with the wave for the nickel catalyst, which makes platinum electrode unusable in catalytic investigations (Fig. 2). [8, 18-20] There is a substantial shift of the hydrogen oxidation potential to the negative potentials compared with neutral systems, because of the amines present, though it is still not enough to carry on homogeneous hydrogen oxidation.

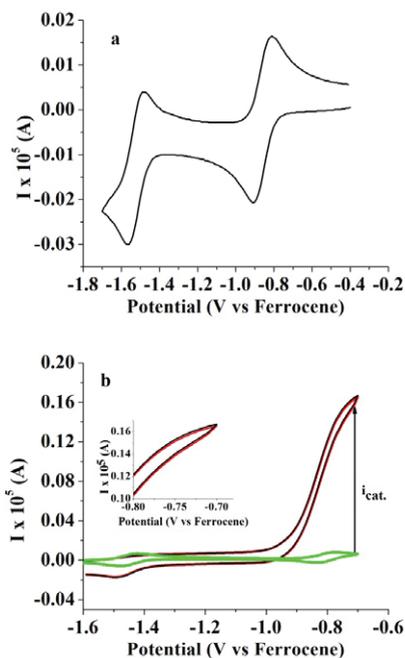


Fig. 1: Cyclic voltammety of $\text{Ni}(\text{PCy}_2\text{Nt-Bu})_2^{2+}$ (a) (0.12 mM) and (b) (0.05 mM) in the presence of hydrogen (1 atm) and presence (black and red line) and absence (green line) of 15 mM TEA; inset is an enlarged version of the catalytic current at two different electrodes. Scan rate: 0.05 V s^{-1} ; red line corresponds with a carbon electrode and black line with gold electrode; solvent: benzonitrile.

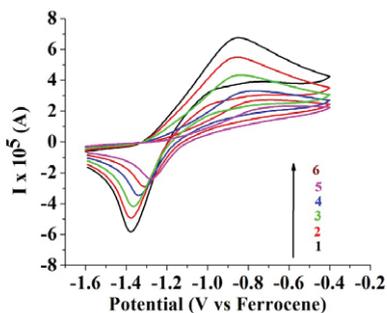


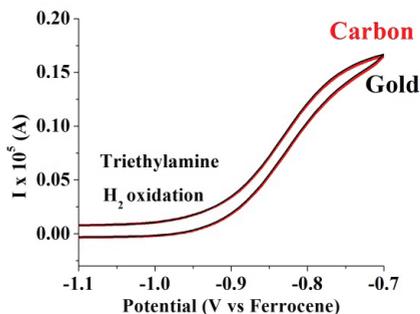
Fig. 2: Cyclic voltammograms showing the passivation of a platinum electrode with consecutive scan in the presence of 50 mM triethylamine; scan rate: 0.1 V/s , solvent: benzonitrile.

4. Conclusions

The current work demonstrates that gold electrode is a suitable material for homogeneous hydrogen oxidation in anhydrous solvents, which is very important in case of surface modification studies and kinetics investigations. This can allow achieving application of the nickel catalysts and materials of other nonprecious materials like iron, which can be a viable alternative for commonly applied heterogeneous catalysts such as platinum. Further efforts will be directed to obtain surface modification of gold electrodes to transform currently synthesized homogeneous solution catalysts to the solid catalysts ready to be used in fuel cells. Final goal is to obtain a surface attached catalyst that demonstrates strong catalytic activity in aqueous systems.

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TOC Figure

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