Novel Ni^{2+} complexes as molecular catalyst prototypes for the hydrogen evolution reaction

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The challenge of combining the power supply capacity that meets the ever-increasing global demand with the concept of sustainability and environmentally friendly power production has lead to extensive researches on alternative energy sources[1]. Among them, electrocatalytically generated hydrogen figure as one of the most attractive options due to its purity, easiness of storage and non-carbon source. However, to facilitate the integration of this technology in the energy matrix, cheaper and more efficient catalysts are required[2]. Nickel complexes are among the best molecular catalysts being evaluated[3]. In this work we report on the evaluation of two novel Ni^{2+} complexes, labeled as [Ni(pymimi)$(H_2O)_2$Cl]Cl (**1**) (pymimi = *N*-((1-methyl-1*H*-imidazol-2-yl)methylene)-2-(pyridin-2-yl)ethanamine) and [Ni(hismima)$(H_2O)_2$Cl]Cl (**2**) (hismima = 2-(1H-imidazol-4-yl)-N-((1-methyl-1H-imidazol-2-yl)methyl)ethanamine), as potential catalyst prototypes for hydrogen evolution reaction.

Complexes **1** and **2** were obtained as previously reported[4,5] and used for further analyses only as crystalline samples. To assess the redox and catalytic behavior of **1** and **2**, cyclic voltammetry (CV) experiments were performed in a standard three electrodes cell (WE: glassy carbon, CE: platinum wire, RE: Ag/AgCl) using TBAPF6 (0.1 mol L^{-1}) as electrolyte, acetic acid (HAc) as the proton source, and complexes concentration of 10^{-3} mol L^{-1}, in CH3CN. Preliminary results show that **1** and **2** are catalytic (Figure 1), as evidenced by the increase of current peak upon the addiction of increasing equivalents of HAc. The overpotential calculated considering the homoconjugation effect was 638 mV vs Fc^+/Fc for complex **1** and 519 mV vs Fc^+/Fc for complex **2**.

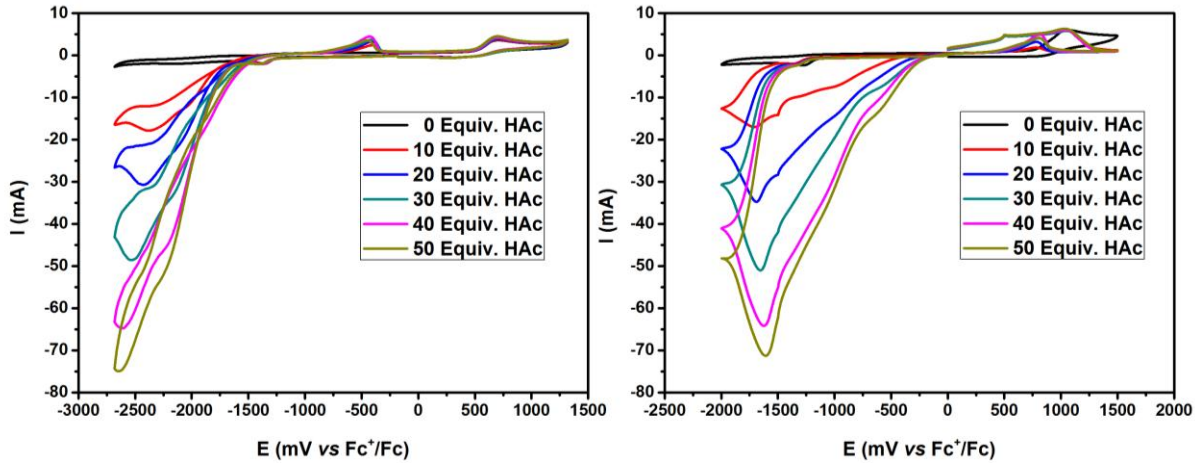

Figure 1. CV experiments of H_2 generation catalyzed by **1** (left) and **2** (right).

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