# Title: In situ X- ray Absorption Spectroscopy and X-ray Photoelectron Spectroscopic studies of $[Ni(II)(P^{Cy}_2N^{Gly}_2)]^{2+}$ and $[Ni(II)(P^{Cy}_2N^{Phe}_2)]^{2+}$

Karolina Anna Lewandowska, Wendy J. Shaw, Serena DeBeer, Olaf Rüdiger
karolina.lewandowska@cec.mpg.de

The consumption rate of fossil fuels is unsustainable. Therefore, it is imperative to find a $CO_2$ neutral energy economy, based on renewable energy sources using earth-abundant metals as catalysts. In this respect, $H_2$ has been proposed as an ideal energy vector.

The synthetic complexes $[Ni(II)(P^{Cy}_2N^{Gly}_2)_2]^{2+}$ and $[Ni(II)(P^{Cy}_2N^{Phe}_2)_2]^{2+}$ are among the most efficient molecular catalysts for $H_2$ production and oxidation, operating at high turnover frequencies ($60s^{-1}$) and low overpotential when small amino acids with $H^+$ transfer capabilities are used as substituents on the pendant amine.[1, 2] The complexes are synthesized as a square-planar $Ni^{2+}$ complexes, which can be reduced by $H_2$ to form tetrahedral $Ni^0$ species with protonated amines.

In order to gain structural and electronic information of the changes taking place at the metal and the coordination sphere, the possibilities of combining electrochemistry and X-ray spectroscopic studies of catalysts involved in $H_2$ evolution and oxidation is being explored.

Electrochemical studies of the immobilized catalyst allow an accurate determination of the overpotential and catalytic activity of complexes, as well as how the systems behave towards inhibitors like $O_2$ or CO or the stability under reaction conditions. Nevertheless, electrochemistry only provides activity measurements. The characterization of catalyst electronic structure before, during, and after the reaction is important for the fundamental understanding of materials performance and stability.

Herein, the results of operando electrochemistry studies (both in electrochemical gas and liquid phase) will be presented together with the simultaneous near ambient pressure XPS (NAP-XPS) and Ni L-edge XAS studies.

[1] P. Rodríguez-Maciá, N. Priyadarshani, A. Dutta, C. Weidenthaler, W. Lubitz, W. J. Shaw, O. Rüdiger, *Electroanalysis* **2016**, *28*, 2452-2458.
[2] P. Rodriguez-Macia, A. Dutta, W. Lubitz, W. J. Shaw, O. Rudiger, *Angew Chem Int Ed Engl* **2015**, *54*, 12303-12307.