

An *ex situ* near edge X-ray absorption fine structure spectroscopy study of metal phthalocyanine catalysts for CO₂ reduction

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The electrochemical reduction of CO₂ is a process that has attracted considerable attention due to the combined benefits associated with the environmental remediation of CO₂ and the production of valuable feedstock materials (e.g. CO) for the production of liquid fuels [1]. We have been studying the use of molecular catalysts such as metal phthalocyanines (MPc) as desirable candidates for CO₂-to-CO electrochemical catalysis as they can be tuned to achieve high activity and selectivity over proton reduction. In particular, iron phthalocyanine (FePc) is particularly interesting because the Fe(0) centre can donate electrons in the activation of CO₂ molecules and exhibits a relatively low onset potential for CO₂ reduction when compared with other metal phthalocyanine systems.

Recently, we observed that the addition and self-assembly of metal-oxide nanoclusters (MO_x, where M = Ni or Co) on FePc catalysts can result in improved catalytic performance compared to the neat material [2]. *Ex situ* near edge X-ray absorption fine structure (NEXAFS) measurements were performed on the catalyst materials as a function of applied potential during CO₂ reduction. Remarkably, the NEXAFS investigation revealed that at certain potentials, electrochemical substitution occurs between the active iron centre in FePc with the Ni or Co from the MO_x nanoclusters. In this presentation, details of the *ex situ* NEXAFS investigations will be presented, in addition to transmission electron microscopy, atomic force microscopy and electrochemical results that demonstrate improved electrocatalytic performance.

References:

[1] Wilhelm D., Simbeck A., Karp R., Dickenson R., Fuel Process Technol. **71**, 139 (2001).

[2] Cheng Y., Veder J.-P., Thomsen L., Zhao S., Saunders M., Demichelis R., Liu C., De Marco R., Jiang S.P., J Mater. Chem. A **6**, 1370 (2018).

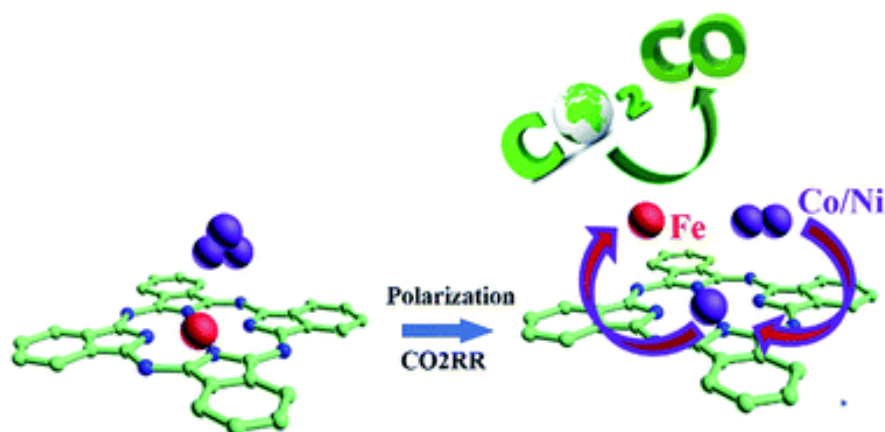


Figure 1: Schematic illustration of CO₂ reduction at a MO_x (where M= Ni or Co)/iron phthalocyanine catalyst electrode.