

# Exploring Oxygen Reduction Reaction at Metal Porphyrins Using Electrochemical Scanning Tunneling Microscopy: a Different View of Electrocatalysis

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ed in video conferenza al link <https://zoom.us/j/85388390096>

password: seminar1

## Abstract

Electrochemical scanning tunnelling microscopy (EC-STM) has recently attracted significant interest due to its unique capability to directly probe matter at the single-atom level under *in operando* conditions. EC-STM combines a scanning tunnelling microscope with a potentiostat, allowing it to monitor and visualize electrochemical processes occurring at a selected working electrode. Therefore, EC-STM can in principle be employed as a *in operando* characterization technique for numerous fundamental electrochemical reactions, in particular  $O_2$  reduction reactions (ORR). The growing interest in developing macroscopic materials with single-atom dispersed catalytic centers has made EC-STM a suitable technique for exploring model systems. Single-atom catalysts are easier to fabricate and analyze in such systems, and EC-STM enables researchers to investigate their properties with high precision and accuracy. For example, M-N-C single site (M = Fe, Co, Mn, etc.) catalysts have emerged as a highly promising alternative to Pt group metals for various electrocatalytic reactions, including ORR. While M-N<sub>x</sub> sites have demonstrated exceptional catalytic properties, there remains a lack of understanding regarding the precise configuration of M-N<sub>x</sub> single sites

during the catalytic process. To address this challenge, metal porphyrins have been identified as valuable model systems for simulating M-N<sub>4</sub> sites [1-3]. In this study, we utilized EC-STM to investigate ORR at metal-centered octaethylporphyrins in potentiodynamic conditions with the aim of monitoring the active site appearance during the electrocatalytic process.

Consistent with the Sabatier principle, an effective catalyst must bind reactants neither too strongly nor too weakly, and the same principle applies to reaction products. Applying this concept to the investigated metal porphyrins, we found that the EC-STM profile of the active site ( $\Delta Z$ ), which is dependent on the local electronic structure, provides a good representation of M-O<sub>2</sub> adsorption. By correlating  $\Delta Z$  with a general electrocatalytic descriptor such as the half peak current ( $i_{p/2}$ ), we observed a Volcano-like trend.

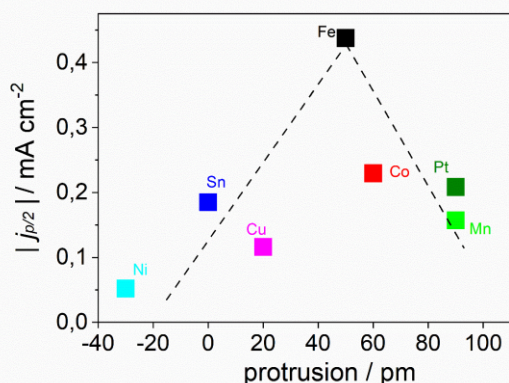


Figure 1. Correlation of the STM revealed protrusion and the half-peak current for part of the investigated metal porphyrins.

[1] A. Facchin, C. Durante, *Adv. Sustain. Syst.* **2022**, 2200111

[2] A. Facchin, M. Zerbetto, A. Gennaro, A. Vittadini, D. Forrer, C. Durante, *ChemElectroChem* **8** (2021) 2825.

[3] A. Facchin, T. Kosmala, A. Gennaro, C. Durante, *ChemElectroChem* **7** (2020) 1431.

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