

Doctoral Dissertation  
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# Unraveling CO<sub>2</sub> Reduction Mechanisms on Selective Electrocatalysts: Computational Insights for Efficient Valorization

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## Abstract

The increasing concentration of CO<sub>2</sub> in the atmosphere due to anthropogenic emissions has led to an environmental crisis, prompting a search for sustainable strategies to recycle CO<sub>2</sub> into valuable products. One of the most challenging tasks for scientists is to convert CO<sub>2</sub> into renewable chemicals and fuels through alternative routes that are efficient, economical, and environmentally friendly.

The electrochemical reduction of CO<sub>2</sub> is a promising pathway towards carbon neutrality as it improves CO<sub>2</sub> conversion efficiency and selectivity and can be coupled with alternative energy resources. However, the main obstacle is the development of robust, active, and selective electrocatalysts for CO<sub>2</sub> reduction reactions (CO<sub>2</sub>RR), which can produce desirable products and avoid competitive side reactions, such as the hydrogen evolution reaction (HER). As a result, significant research efforts have been directed towards designing highly selective and novel electrocatalysts that involve low overpotentials.

The electrochemical reduction of CO<sub>2</sub> requires effective performing electrocatalysts, but interpreting experimental measurements and predicting the relationship between the structure and activity of an electrocatalyst is challenging. In this regard, first principle calculations are a powerful tool to get a better insight into electrocatalytic materials working in synergy with experimental research.

In this work, *ab initio* methods based on Density Functional Theory (DFT) calculations have been used to analyse materials at an atomic level and predict optimal properties for CO<sub>2</sub> conversion. In computational electrochemistry, the two main strategies to study an electrochemical system are based on the use of thermodynamic and kinetics analysis. This thesis employs both approaches to perform theoretical calculations aimed to answer open questions from experimental evidence and provide guidelines for the synthesis of efficient and selective electrocatalysts for CO<sub>2</sub> reduction to valuable products.

In the first part of the thesis, the SnO<sub>2</sub> and ZIF-8 electrocatalysts, which are known to be selective towards formic acid (HCOOH) and carbon monoxide (CO), respectively, have been investigated from a

thermodynamic perspective.

Firstly, the active phase of SnO<sub>2</sub> electrode in electrocatalytic CO<sub>2</sub> reduction to HCOOH is unknown. The goal of this study was to determine the active surface structure of the electrode, metallic Sn(0) or oxide Sn(II), and how the selectivity and reactivity towards CO<sub>2</sub>RR change with surface reduction degree. At the first stage of the reaction, results show that the SnO<sub>2</sub> surface is inactive for CO<sub>2</sub>RR and HER, but it self-reduces upon an applied potential until it exposes a metallic tin layer. The formation of a thin Sn(0) layer turns the electrode selective for HCOOH. Higher bias results in an increased thickness of the metallic phase, which causes a loss of selectivity. These findings explain the experimental observations that both metallic Sn and oxidized SnO<sub>2</sub> phases are revealed during experiments at electrocatalyst working condition.

Afterward, theoretical calculations were used to study ZIF-8 as an electrocatalyst for CO<sub>2</sub> capture and reduction to CO and present theory-guided synthesis of the material. The work aimed to predict the active site and the reaction mechanism for this conversion, as well as to tune the efficiency and selectivity of the electrocatalyst. The surface termination of ZIF-8 was found to expose imidazole-imidazolate pairs, which were proposed as the active site for CO<sub>2</sub> reduction. By incorporating carbon nanotubes (CNTs) as a support and reducing the size of the catalyst, an enhancement in selectivity was observed. The computational guidelines provided were validated through following experimental investigation.

The use of a thermodynamic approach in electrocatalysis without accounting for kinetic barriers in some cases may fail to give a correct description of the electrochemical processes occurring at a given catalyst surface. For example, Ag and Zn electrodes experimentally produce CO, but should produce HCOOH and H<sub>2</sub> according to the DFT thermodynamics. This suggests that kinetics controls the reaction mechanism in these electrodes.

In this perspective, the last part of the works was focused on the kinetics investigation of CO<sub>2</sub>RR and HER on Ag and Zn metal electrodes calculating kinetic energy barriers of competing reaction mechanisms at different potentials values. The Tafel- and Heyrovsky mechanisms for CO and HCOOH (or formate) production were considered for CO<sub>2</sub>RR, while for HER the Volmer-Heyrovsky mechanism. The estimated activation energy barriers showed that the first proton-electron transfer of Heyrovsky mechanism for CO<sub>2</sub>RR is the rate determining step, leading then to CO. In contrast with experiments, the results also show that CO<sub>2</sub>RR is generally favoured over HER for the entire explored range of potentials, suggesting that other catalytic sites, like structural defects at the surface of the electrode, are possibly selective for HER.