Electrochemical Liquid-Phase TEM for Operando Characterization

Setup Optimization and Experimental Assessment

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ABSTRACT

Achieving a sustainable energy transition and climate change mitigation requires profound changes in the way energy is produced, stored, and utilized. Electrochemical energy conversion and CO_2 valorization play a pivotal role in this transformation, as they enable the direct coupling of renewable electricity with chemical processes, producing fuels and industrial feedstocks while minimizing carbon emissions. However, many key reactions involved in this transition are thermodynamically unfavorable under ambient conditions, and thus require significant external energy input. To overcome these limitations and guide product selectivity, electrocatalysts are employed to accelerate the conversion of molecules such as water, and carbon dioxide into valuable compounds. Among the most promising processes, the electrochemical CO_2 reduction reaction (CO_2RR) is uniquely capable of both valorizing CO_2 and generating added-value chemicals, thereby supporting the development of carbon-neutral value chains. Despite significant progress in catalyst development, the mechanisms governing activation, possible restructuring, and stability under operating conditions remain unclear. Catalysts frequently undergo dynamic morphological, structural and chemical transformations after potential / current application, that strongly affect their performance. Therefore, advanced *operando* characterization methods are essential to bridge the gap between catalyst modification at the nanoscale and its behavior in laboratory-scale electrochemical experiments.

Electrochemical liquid-phase transmission electron microscopy (EC-LPTEM) represents a powerful platform for real-time observation at the nanoscale in liquid environment under electrochemical stimulation. Conventional EC-LPTEM setup face challenges such as electrolyte confinement, gas bubbles accumulation, and limited electrochemical control, which sometimes restrict its applicability, especially in the electrocatalysis framework. In particular, CO_2RR requires highly negative potentials that generate, in some cases, high amount of gaseous products, posing a significant obstacle to stable *operando* measurements.

This thesis addresses these challenges by optimizing the EC-LPTEM cell in terms of fluidic configuration and electrochemical response, enabling reliable *operando* studies of catalysts for CO_2RR.

A redesigned flow architecture featuring a bypass channel around the working electrode was tested to demonstrate its capability in enhancing fast product removal and continuous supply of fresh electrolyte, thus suppressing gas-induced electrodes dewetting and expanding the accessible potential window. These improvements allowed CO_2RR experiments to be carried out in a cell fully filled with electrolyte. To validate the new flow architecture, an *operando* experiment has been performed on a

Cu-Based catalyst. *Operando* observations revealed dissolution-reprecipitation dynamics triggered upon electrochemical stimulation at current densities relevant for laboratory-scale operation (up to -20 mA cm^{-2}), while posing some open questions on the electrochemical reliability of the reference electrode in the EC-LPTEM cell.

To address this problem, avoiding electrochemical measurements' instabilities and preventing unwanted side gaseous products formation, Pd nanostructuring of the reference and counter electrodes was implemented, in order to greatly increase their electroactive surface area. This optimization improved reference stability and counter electrode functionality, leading to a more reproducible and reliable electrochemical control within the EC-LPTEM cell.

Recognizing that the confined geometry of EC-LPTEM cell deviates significantly from bulk electrochemical systems, numerical simulations using COMSOL Multiphysics were performed to quantify confinement-induced effects on the electrochemical response of the cell. The model demonstrated that the extremely thin electrolyte layer strongly alters mass transport regimes, increases iR drop, and induces non-uniform current distribution across the working electrode. These insights offer essential guidelines for accurate interpretation of experimental results and for future improvements of the EC-LPTEM cell design.

Overall, this thesis provides a robust methodology to extend EC-LPTEM analysis to other electrocatalytic reactions relevant to the energy transition, enabling direct visualization of catalyst evolution under realistic operating conditions. This study provides a detailed understanding of how to decouple the influence of EC-LPTEM cell from the catalyst's intrinsic response under external stimulation.

By deepening the understanding of structure-catalytic activity relationships at the nanoscale, these advances contribute to the rational design of more efficient, selective, and durable catalysts for sustainable electrochemical energy conversion.