

# Operando Spectroscopic and Electrokinetic Analysis of Formic Acid Oxidation on Copper Surfaces

---

## Abstract

---

Formic acid oxidation has garnered significant attention in recent years due to its potential applications in fuel cells and green chemistry. Investigating the reaction mechanisms and kinetic properties of this process on copper surfaces is crucial for developing more efficient catalysts. This study employs operando spectroscopic techniques, including infrared (IR) and X-ray absorption spectroscopy (XAS), alongside electrokinetic analysis to unravel the complexities of formic acid oxidation on copper electrodes. The findings illuminate the roles of intermediates, catalytic sites, and the impact of electronic structure on the reaction pathway, providing new insights into optimizing copper-based catalysts for formic acid oxidation.

## Introduction

---

### Background

Formic acid ( $\text{HCOOH}$ ) is a small molecule that has gained significant interest for its application in direct formic acid fuel cells (DFAFCs), an emerging technology for sustainable energy. The electrochemical oxidation of formic acid on metal surfaces, particularly copper, is a pivotal reaction that influences the efficiency and practicality of DFAFCs. Copper, being an affordable and abundant metal, holds promise as a catalyst, yet its performance is hindered by incomplete understanding of the reaction mechanisms and catalyst surface interactions.

### Objective

This paper aims to elucidate the mechanisms of formic acid oxidation on copper surfaces via an integrated approach using operando spectroscopic techniques and electrokinetic analysis. The study seeks to identify catalyst intermediates, assess the catalytic efficiency of copper surfaces, and determine how electronic properties influence the reaction pathway.

## Experimental Methods

---

### Materials and Electrodes

High-purity copper foils were used as electrodes. These were prepared through mechanical polishing and subsequent electrochemical cleaning. Formic acid solutions of varying concentrations were prepared using ultrapure water and reagent-grade formic acid.

### Electrochemical Setup

Cyclic voltammetry (CV) and chronoamperometry were employed to monitor the electrochemical behavior of formic acid oxidation on copper. An Ag/AgCl electrode served as the reference electrode, while a platinum wire was used as the counter electrode.

# Operando Spectroscopic Techniques

## Infrared Spectroscopy (IR)

Operando IR spectroscopy was utilized to detect surface intermediates and adsorbates during the oxidation reaction.

## X-ray Absorption Spectroscopy (XAS)

Operando XAS provided insights into the oxidation states and local electronic structure of the copper catalyst.

## Electrokinetic Analysis

The kinetics of formic acid oxidation were analyzed using linear sweep voltammetry (LSV) and Tafel plots. Activation energy and exchange current density were determined to understand the reaction energetics and kinetics.

## Results and Discussion

---

### Voltammetric Behavior

Cyclic voltammetry of formic acid on copper surfaces showcased characteristic peaks corresponding to the oxidation process. These peaks provide information on the onset potentials and current densities, indicative of the catalytic activity.

### Identification of Intermediates

Operando IR spectroscopy revealed the presence of distinct intermediates such as formate ( $\text{HCOO}^-$ ) ions and  $\text{CO}_2$  on the copper surface during the oxidation process. The spectra suggest that the reaction proceeds via a dual-path mechanism involving direct oxidation of formic acid to  $\text{CO}_2$  and an indirect path through formate intermediates.

### Electronic Structure and Oxidation States

XAS analysis indicated that copper cycles between  $\text{Cu}(0)$  and  $\text{Cu}(I)$  states during the oxidation process. The presence of  $\text{Cu}(I)$  phases suggests a dynamic restructuring of the catalyst surface, which could influence catalytic performance through electronic and structural modifications.

### Electrokinetic Parameters

Tafel slope analysis and Arrhenius plots provided activation energy values and insight into the rate-determining steps of the oxidation process. The results indicated a lower activation energy for formic acid oxidation on copper compared to other metal surfaces, potentially explaining the observed catalytic behavior.

### Surface Reactivity and Catalyst Stability

Extended chronoamperometry showed that copper surfaces exhibit reasonable stability under continuous operation, though certain degradation pathways, such as surface oxidation and adsorption of poisoning species, were identified. The data suggest that optimizing surface treatments and protective coatings could enhance catalyst longevity.

## Conclusion

---

The integrated analysis combining operando spectroscopic techniques and electrokinetic measurements has provided a comprehensive view of the formic acid oxidation mechanism on copper surfaces. The identification of key intermediates and electronic states informs potential strategies for improving copper-based catalysts. Insights from this study could guide the development of more efficient and durable catalysts for formic acid oxidation, furthering the application of DFAFCs and other green chemistry technologies.

## Acknowledgments

---

The authors would like to acknowledge the support and resources provided by the Institute of Green Chemistry.

## References

---

1. Author A, Author B. Title of the article. Journal Name. Year;Volume(Issue):Page numbers.
2. Author C, Author D. Title of the article. Journal Name. Year;Volume(Issue):Page numbers.
3. and so on.

---

Tables, figures, and additional supplementary information can be embedded as required to further support the findings discussed in the main text.