

Abstract

Exploring the Reaction Mechanism and Electronic, Thermodynamic, and Kinetic Parameters of Electrochemical CO₂ Reduction to CO on a Copper Electrocatalyst Using First-Principle Calculations [†]

Reza Gholizadeh , Blaž Likozar  and Matej Huš 

Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, 1001 Ljubljana, Slovenia

* Correspondence: reza.gholizadeh@ki.si

[†] Presented at the 3rd International Electronic Conference on Processes—Green and Sustainable Process Engineering and Process Systems Engineering (ECP 2024), 29–31 May 2024; Available online: <https://sciforum.net/event/ECP2024>.

Keywords: DFT simulations; CO₂ electrochemical reduction; copper; reaction rate; applied potential; pH



Citation: Gholizadeh, R.; Likozar, B.; Huš, M. Exploring the Reaction Mechanism and Electronic, Thermodynamic, and Kinetic Parameters of Electrochemical CO₂ Reduction to CO on a Copper Electrocatalyst Using First-Principle Calculations. *Proceedings* **2024**, *105*, 20. <https://doi.org/10.3390/proceedings2024105020>

Academic Editor: Juan Francisco García Martín

Published: 28 May 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Introduction: The electrochemical reduction of carbon dioxide (CO₂) to carbon monoxide (CO) is a promising approach to mitigate greenhouse gas emissions and produce valuable chemicals. In this work, we investigate the reaction mechanism and kinetics of electrochemical CO₂ reduction on Cu(100) using density functional theory (DFT) calculations.

Methods: We constructed a four-layer slab of Cu(100) and placed CO₂, H₂O, CO, H, OH, and H₂ as adsorbates on the surface. We calculated the Gibbs free energies, adsorption energies, activation barriers, and reaction rates of all the elementary reactions using DFT and transition state theory. We also modeled the solvation effect by placing a monolayer of H₂O molecules on the catalyst surface.

Results: We found that the most favorable pathway for the electrochemical reduction of CO₂ to CO on Cu(100) involves the transformation of trans-COOH* and its isomerization to cis-COOH*, followed by CO* + OH → CO and CO* + H → CO + H₂O. The calculated rate constants show that CO₂* + H → trans-COOH* is the predominant form of CO₂ activation. We also investigated the effects of a water layer on the CO₂RR-to-CO kinetics. Our results showed that the majority of elementary reactions exhibited altered reaction barriers, emphasizing the profound influence of the water environment on the reaction mechanism. Furthermore, our study on the effects of introducing a layer of water molecules on the CO₂RR-to-CO kinetics showed significant changes in the rates of most elementary reactions, indicating a nuanced interaction between the water molecules and the catalyst surface.

Conclusions: Our DFT calculations provide insights into the reaction mechanism and kinetics of electrochemical CO₂ reduction on Cu(100). The results indicate that copper is a promising electrocatalyst for transforming CO₂RR to CO and highlight the importance of considering solvation effects when modeling electrochemical reactions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/proceedings2024105020/s1>.

Author Contributions: Conceptualization, R.G.; methodology, R.G.; validation, R.G. and M.H.; formal analysis, R.G. and M.H.; investigation, R.G. and B.L.; data curation, R.G.; writing—original draft, R.G.; visualization, R.G.; writing—review & editing, R.G., M.H. and B.L.; supervision, M.H. and B.L.; resources, B.L.; project administration, B.L.; funding acquisition, B.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by EU commission-Horizon 2020 Framework Programme-Marie Skłodowska-Curie Actions (MSCA) Individual Fellowships (IF), grant number 892003. B.L. was funded by the ARRS project J7-4638. M.H. was funded by the ARRS project N1-0303. The APC was funded by National Institute of Chemistry.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available upon request.

Acknowledgments: The Slovenian Research Agency (ARRS) is thanked for providing the infrastructure support (I0-0039) and core support (P2-0152). The authors gratefully acknowledge the HPC RIVR consortium (www.hpc-rivr.si) and EuroHPC JU (eurohpc-ju.europa.eu) for funding this research by providing computing resources of the HPC system Vega at the Institute of Information Science (www.izum.si).

Conflicts of Interest: The authors declare no conflict of interest.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.