

University of Louisville
Department of Chemistry
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Literature Seminar

When: March 7, 2024

Time: 12:00 p.m.

Location: CBL-16

Metal-ion mediated electrocatalytic CO₂ reduction: Mechanistic insights and pathway optimization strategies

Abstract:

Understanding microenvironments at the electrode-electrolyte interface is crucial for understanding the activity and selectivity of electrocatalytic reactions. Recent literature on electrocatalytic CO₂ reduction has revealed that the properties of metal cations in electrolytic solutions have a marked impact on the energetics of CO₂ reduction. There is debate on the origin of the influence of cations on the reduction of CO₂. Common descriptions include cations affecting the local electric field, stabilizing surface intermediates, and buffering the reaction. This seminar will examine recent literature articles that address the mechanistic origin of cations promoting CO₂ reduction. Koper and coworkers use cyclic voltammetry and scanning electrochemical microscopy to investigate the CO₂ reduction reaction on copper, silver, and gold electrodes in the absence and presence of different alkaline metal cations.¹ They reveal that not only do metal cations enhance the reaction, but are necessary for CO₂ reduction to occur on the studied electrode materials. J. Gu and coworkers quantitatively assess the effect of metal cations in electrocatalytic CO₂ reduction using a combination of cyclic voltammetry, simulations, and X-ray diffraction XRD.² Their study highlights that metal cations affect the electric field in the Stern layer and that the concentration of metal cations impacts proton diffusion, determining factors for reaction selectivity. Work by P. Kenis et al. compares the performance of alkaline metal cations with multivalent cations in the CO₂ reduction reaction.³ This study suggests that multivalent cations reduce reaction rates and reaction selectivity compared to monovalent cations due to the formation of metal oxides and hydrides. This collection of literature summaries recent knowledge on the non-innocent role of cations in electrocatalysis and demonstrates that there are several knowledge gaps that remain to be filled.

References:

- (1) Monteiro, M. C. O.; Dattila, F.; Hagedoorn, B.; García-Muelas, R.; López, N.; Koper, M. T. M. Absence of CO₂ Electroreduction on Copper, Gold and Silver Electrodes without Metal Cations in Solution. *Nat. Catal.* **2021**, *4* (8), 654–662.
- (2) Qin, H.-G.; Li, F.-Z.; Du, Y.-F.; Yang, L.-F.; Wang, H.; Bai, Y.-Y.; Lin, M.; Gu, J. Quantitative Understanding of Cation Effects on the Electrochemical Reduction of CO₂ and H⁺ in Acidic Solution. *ACS Catal.* **2023**, *13* (2), 916–926.
- (3) Bhargava, S. S.; Cofell, E. R.; Chumble, P.; Azmoodeh, D.; Someshwar, S.; Kenis, P. J. A. Exploring Multivalent Cations-Based Electrolytes for CO₂ Electroreduction. *Electrochimica Acta* **2021**, *394*, 139055.