University of Louisville
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Literature Seminar

When: September 18, 2023
Time: 3:00 p.m.
Location: CBLL-16

Origin of the C_{2+} selectivity of electrochemical CO_2 reduction on oxide-derived copper electrocatalysts

Abstract:

Research efforts are increasingly focused on solutions for energy storage and distribution due to the impending fossil fuel depletion and the intermittency of renewable energy. The electrochemical CO_2 reduction reaction (CO_2RR) is a promising method to use surplus renewable energy production to convert CO_2 into value-added fuels and chemical feedstocks, while mitigating anthropogenic greenhouse gas emissions. Oxide-derived Cu (OD-Cu) electrocatalysts perform well in the electrochemical CO_2RR, particularly in C–C coupling processes, which is a critical step to produce desirable and energy-dense hydrocarbons and alcohols. However, the role of the different Cu chemical states and the adsorbed intermediates on the selectivity towards C_{2+} products remain controversial. Furthermore, the surface of oxide-derived Cu catalysts has been found to be dynamic and heterogeneous, leading to a complex distribution of molecular intermediates and products. Various analytical experiments have provided valuable insights into CO_2RR, but due to the intrinsic complexity of the electrode-electrolyte interface, static measurements are insufficient to understand dynamic processes, while probing over a large area only provides ensemble-averaged information and cannot reveal spatial heterogeneity. Therefore, in order to gain a deeper understanding of electrocatalysis, *in situ* and *operando* characterization techniques are essential. In this seminar, recent discoveries in the origin of selectivity of C_{2+} products of the electrochemical CO_2RR on OD-Cu will be discussed through three examples from the literature. First, Weckhuysen and co-workers[1] combined spatially- and temporally-resolved surface-enhanced Raman scattering spectroscopy and mapped local heterogeneities in the OD-Cu catalyst surface through the observed molecular intermediates, attributing the increased C_{2+} selectivity of OD-Cu to flatter regions in the electrode. On the other hand, Han and co-workers,[2] through *ex situ* electron microscopy and *operando* spectroscopy experiments, investigated the surface species and chemical states of the OD-Cu catalyst during the reaction and attributed the enhanced C_{2+} selectivity to heterogeneous CO adsorption sites. Finally, Chen and co-workers[3] used time-resolved X-ray absorption spectroscopy experiments to understand the correlation between the oxidation state of OD-Cu and reaction selectivity. Each work characterized CO_2RR in OD-Cu in different and complementary ways, but the different conclusions demonstrate how benchmarks and further studies are required to better understand this, and other electrochemical systems.

References:

(1) An, H.; de Ruiter, J.; Wu, L.; Yang, S.; Meirer, F.; van der Stam, W.; Weckhuysen, B. M. Spatiotemporal Mapping of Local Heterogeneities during Electrochemical Carbon Dioxide Reduction. *JACS Au* **2023**, *3* (7), 1890–1901. https://doi.org/10.1021/jacsau.3c00129.

(2) Chen, C.; Yan, X.; Wu, Y.; Liu, S.; Sun, X.; Zhu, Q.; Feng, R.; Wu, T.; Qian, Q.; Liu, H.; Zheng, L.; Zhang, J.; Han, B. The *in situ* Study of Surface Species and Structures of Oxide-Derived Copper Catalysts for Electrochemical CO_2 Reduction. *Chem. Sci.* **2021**, *12* (16), 5938–5943. https://doi.org/10.1039/D1SC00042J.

(3) Lin, S.-C.; Chang, C.-C.; Chiu, S.-Y.; Pai, H.-T.; Liao, T.-Y.; Hsu, C.-S.; Chiang, W.-H.; Tsai, M.-K.; Chen, H. M. Operando Time-Resolved X-Ray Absorption Spectroscopy Reveals the Chemical Nature Enabling Highly Selective CO_2 Reduction. *Nat. Commun.* **2020**, *11* (1), 3525. https://doi.org/10.1038/s41467-020-17231-3.