

Advanced Electrochemical Investigation of Covalent Organic Framework Electrocatalysts

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More efficient catalysts for green and renewable energy technologies have to be developed to increase the economic feasibility of these applications. This driving force is pushing research towards the synthesis of increasingly complex (nano)materials. Due to their stable and highly porous structures, covalent organic frameworks (COFs) could play an important role in the future as alternatives to traditional platinum group metals based electrocatalysts in several reactions. [1] However, accurately determine the catalytic activity of these materials and the underlying reaction mechanism is not trivial. Traditionally electrocatalysis are tested in their activity by immobilizing a multitude of nanoparticles on an inert support. However, this often leads to a non-trivial structure-activity determination, as the current response is given by the sum of each individual contribution, and mass transport and resistive effects can alter the results obtained. [2] Different strategies have to be developed to reliably investigate the catalytic activity of complex nanomaterials. This work aims to showcase advanced techniques for the investigation of the electrochemical properties of COF. Spectroelectrochemical methods like surface-enhanced infrared absorption spectroscopy (SEIRAS) and differential elemental mass spectroscopy (DEMS) are used to investigate the activity and selectivity of different COF films for the CO₂ reduction reaction. Directly probing the adsorption behavior of distinct species and intermediates and online product detection allow to obtain key insight on underlying reaction mechanism. [3] Single entity electrocatalytic experiments, as nano-impacts and single nanoparticle voltammetry, [4] are instead used to investigate the oxygen evolution reaction at individual COF-366-Co nanoparticles allowing to develop more accurate information on the catalytic activity and stability of this material.

[1] K. Geng, T. He, R. Liu, S. Dalapati, K. T. Tan, Z. Li, S. Tao, Y. Gong, Q. Jiang, D. Jiang; *Chem. Rev.* 2020, **120**, 8814–8933 DOI: 10.1021/acs.chemrev.9b00550.

[2] P. Cignoni, N. Blanc, K. Tschulik; *Curr. Opin. Electrochem.*, 2023, **38**, 101225, DOI: 10.1016/j.coelec.2023.101225.

[3] M. Dunwell, Q. Lu, J. M. Heyes, J. Rosen, J. G. Chen, Y. Yan, F. Jiao, B. Xu; *JACS* 2017, **139**, 3774–3783, DOI: 10.1021/jacs.6b13287.

[4] M. Azimzadeh Sani, K. Tschulik in *Frontiers of Nanoscience*, Elsevier, 2021, 203–252, DOI:10.1016/B978-0-12-820055-1.00007-1