P2.3 Theoretical modelling of electrochemical CO_2-to-oxalate conversion

Topic and overall goal. Molecular electrocatalysis will be explored for CO_2-to-oxalate conversion following the strategy presented in TP1.[1] The electrochemical approach allows for continuous adjustment of the driving force and a more precise control of the selectivity of the reductive processes,[2] but alternative pathways may become accessible implying the need for mechanistic understanding of underlying processes. This project is devoted to the theoretical modelling of the elementary steps of electrochemical CO_2-to-oxalate conversion using transition metal catalysts.

Specific aims and work plan. The project will start with investigation of the cathodic activation of TM catalysts. Suitable candidates from TP1 as well as from existing libraries at our institutions will be applied and carefully studied by means of optimally-tuned long-range corrected functionals that have been successfully utilized previously for a series of Ir and Fe catalysts.[3,4] By non-empirical tuning to fulfill the Koopmans' theorem for DFT, the asymptotic behavior and ionization properties of the functional are corrected. This implies a reliable description of all properties connected to changes in outer electron shells, which are highly relevant for electrochemical applications. The capabilities of optimally tuned DFT for metal-organic catalysts within the project will be carefully tested based on comparison with available spectroscopic information. For several compounds, multireference calculations will be performed to validate the approach.

As a starting point to describe electrochemical C-C bond formation, the cathodic conversion of bis(alkoxycarbonyl) and bis(hydroxycarbonyl) model intermediates as well as oxalate-bridged binuclear intermediates will be addressed. The UV-Vis- and IR-spectra will be simulated to assign the results of spectroelectrochemical data and to suggest the intermediates produced electrochemically. These studies are intended to gather knowledge about the individual steps, which will later be useful in the development and optimization of electrocatalytic processes (P2.1 and P2.2).

Comprehensive mechanistic analysis of the individual steps will be conducted by combining quantum chemical calculations, electroanalytical techniques and spectroelectrochemistry. Possible reaction paths including energy profiles, search for transitions states and identification of the rate-defining steps will be analyzed by joint efforts from the theory and experimental sides.

Based on gained mechanistic insights from the work on model electrochemical systems, further optimization of metal and ligand of TM catalysts will be performed. The key descriptors for an appropriate selection of candidates will be chosen by theoretical and experimental analysis of test catalysts. The uptime goal is a theoretical pre-screening of suggested TM complexes, such that only selected compounds must be synthesized.

Connection within the RTG. Synthesis and characterization of organometallic compounds and catalytic intermediates will be performed within electrocatalytic and spectroelectrochemical subprojects of TP2 in close collaboration with TP1 (dealing with similar catalysts but for thermochemical applications), while spectroscopic analysis of the electrochemical processes will be conducted within P2.4 (UV-Vis and FTIR SEC), and P2.5 (TR-UV-Vis SEC).

This project is closely interlinked with other subprojects of TP2. The results achieved in one subproject will be applied and analyzed by the other projects to achieve the synergetic effect of a multiple-approach collaboration.

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1 H. Liang, T. Beweries, R. Francke, M. Beller, *Angew. Chem. Int. Ed.* **2022**, e202200723.

2 R. Francke, B. Schille, M. Roemelt, *Chem. Rev.* **2018**, *118*, 4631–4701.

3 O. Bokareva, T. Möhle, A. Neubauer, S. Bokarev, S. Lochbrunner, O. Kühn. *Inorganics* **2017** 5, 23.

4 S. Fischer, O. Bokareva, E. Barsch, S. Bokarev, O. Kühn, R. Ludwig, *ChemCatChem* **201**6, 8, 404–411.