P2.4 Combination of IR/UV-vis SEC with electroanalytical tools for mechanistic studies

Topic and overall goal. Electrochemical approaches toward CO_2-to-oxalate conversion will be investigated building on the strategy described in TP1.[1] In contrast to the classical homogeneous catalytic approach, electrochemistry allows for continuous adjustment of the driving force (electrode potential vs. redox potential of the stoichiometric reductant).[2] Aside from a more precise control of the selectivity of the reductive processes, alternative pathways may thus become accessible. With the aim of establishing an electrocatalytic process (Figure A), the cathodic activation of TM catalysts for subsequent reaction with CO_2 will be explored using spectroelectrochemical and electroanalytical tools.

Specific aims and work plan. The project will start with investigation of the key steps of targeted catalytic schemes in collaboration with P2.1. For this purpose, suitable catalysts and pre-formed intermediates from TP1 as well as from existing libraries at our institutions will be used. The ensuing development and optimization of electrocatalytic processes (P2.2) will be accompanied by SEC analysis for reaction monitoring.[3] Comprehensive mechanistic studies will be conducted by combining SEC with electroanalytical techniques and quantum chemical calculations (the latter in collaboration with P2.3). Promising pre-catalysts and intermediates will be subjected to cyclic voltammetry (CV) and UV-vis-SEC for reaction monitoring. For the latter, a commercial optically transparent thin layer electrode (OTTLE) cell will be used.[4] The measurements in the optical domain can be complemented by *in situ* IR-SEC including step scan techniques which allows to identify appearing species by their characteristic IR spectra. For this purpose, a custom-made set-up for measurements in the external reflectance mode is available (see Figure B).[5] Chemometric analysis of the spectroscopic data (in collaboration with TP4) will render pure component spectra as well as concentration profiles of the participating species, providing valuable information on the mechanisms at work (including catalyst deactivation).

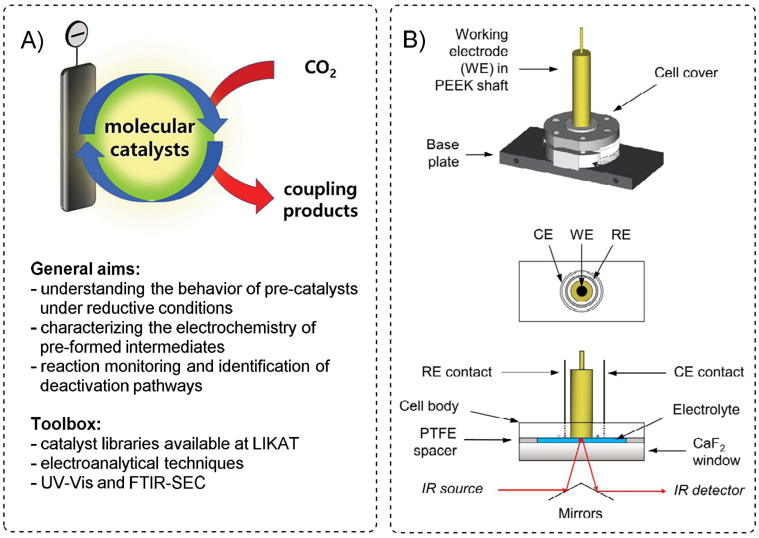

Figure P2.4. Summary of the combined spectroelectrochemical-electroanalytical approach.

Connection within the RTG. Studies on organometallic compounds and pre-formed catalytic intermediates are planned in close collaboration with TP1, P2.1, and P2.2. Spectroscopic analysis of the electrochemical processes will be conducted in collaboration with P2.5 (TR-UV-Vis SEC). The electrocatalytic and spectroelectrochemical studies will be complemented by quantum chemical modelling (P2.3) and chemometric analysis of the spectroscopic data (TP4).

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