

P2.5 Time-resolved UV-vis Spectroelectrochemistry

Topic and overall goal. Time-resolved UV-vis spectroelectrochemistry (TR-UV-vis-SEC) is a powerful tool to investigate the processes taking place in electrocatalysis and to obtain insight into the mechanisms. However, in conventional TR-UV-vis-SEC the temporal resolution and the detection of short-lived species generated at the working electrode is limited by the volume segment, which is probed by the light beam of the spectroscopic instrument, and related diffusion effects.¹ It is therefore difficult to observe species with a lifetime in the millisecond range or below. Based on literature-known approaches that have been used for TR-SEC analysis of stable electro-generated species,² we want to develop a setup that can detect short-lived species in a very confined range close to the electrode. The setup will then be used to analyze the cathodic activation of TM catalysts and the cathodic conversion of bis(alkoxycarbonyl) and bis(hydroxycarbonyl) complexes, which are investigated in TP2. The achieved developments will ultimately provide new insights into the electrocatalytic systems studied in TP2.

Specific aims and work plan. The aim of the PhD project is to develop and apply a setup for time-resolved UV-vis-spectroelectrochemistry with a time resolution of about a microsecond. The goal is to monitor the appearance of short-lived intermediates during the reactions, thereby gaining insights into the mechanisms at work. This should be possible since metal complexes typically exhibit changes in their absorption spectra as soon as variations in their electronic structure take place. In the field of homogeneous electrocatalysis, however, preliminary works are not available. This may be ascribed to the fact that the relevant processes take place exclusively in the reaction-diffusion layer, which is in the order of $\sqrt{D/2k_{cat}}$ (D = diffusion coefficient of the catalyst) and thereby constricted compared to the classical diffusion layer.³ Depending on the rate of the catalytic process (reflected by the rate constant k_{cat}), the film thickness is a few to several tens of μm . To address the issue of spatial confinement, we will use a laser-like white light continuum for probing, which is provided by an ultrafast laser system. The continuum will be focused down to a spot size of a few 10 μm and applied in a parallel transmission geometry close to the electrode. The reaction dynamics will be triggered by a step-like voltage change. The setup will be based on an existing regenerative Ti:sapphire amplifier system. The continuum is generated by focusing a fraction of the output of the Ti:sapphire system into a rotating CaF_2 -disc. Its spectrum spans from 400 nm to 700 nm.⁴ Due to its laser-like propagation properties, its rather high intensity, and intrinsically extreme short pulse duration, it is superior to other light sources and allows for highly sensitive absorption measurements with an excellent time resolution. After passing the cell, it will be detected for each laser shot separately by an available prism-based spectrometer. Together with the confinement to the reaction-diffusion layer in front of the electrode, this should allow for the sensitive detection of short-lived species in electrocatalytic systems.

A further challenge that is expected in view of time scales is the response time of the working electrode. The minimum time scale of a step experiment is reflected by the RC time constant,¹ which is in the order of 30 μs for regular setups with planar electrodes having diameters in the mm range. The resulting feasible time resolution would be about $5 \cdot \text{RC} = 150 \mu\text{s}$. Therefore, a suitable SEC cell will be constructed by optimizing the electrode surface area, the electrode configuration and the conductivity of the electrolyte.

TR-UV-vis-SEC will firstly be applied to the cathodic activation of TM catalysts. In this case we will be able to follow the different oxidation states of the metal complexes, since they typically exhibit characteristic absorption bands due to optical metal-to-ligand or ligand-to-metal charge transfer transitions which are sensitive to the charge of the metal atom and of the involved ligand.

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- 1 a) J. J. A. Lozeman, P. Führer, W. Olthuis, M. Odijk, *Analyst* **2020**, 145, 2482. b) A. J. Bard, L. R. Faulkner, "Electrochemical Methods – Fundamentals and Applications", 2nd Edition (2000), John Wiley & Sons.
 - 2 a) L. Zedler, A. K. Mengele, K. M. Ziems, Y. Zhang, M. Wächtler, Stefanie Gräfe, T. Pascher, S. Rau, S. Kupfer, B. Dietzek, *Angew. Chem. Int. Ed.* **2019**, 58, 13140 – 13148. b) E. Lins, S. Read, B. Unni, S. M. Rosendahl, I. J. Burgess, *Anal. Chem.* **2020**, 92, 6241-6244.
 - 3 J.-M. Savéant, C. Costentin, *Elements of Molecular and Biomolecular Electrochemistry*, 2nd Edition (2019), Wiley.
 - 4 A. Pöpcke, A. Friedrich, and S. Lochbrunner, *J. Phys.: Condens. Matter* **2020**, 32, 153001.

Accordingly, we expect after the voltage step a fast change in the spectra due to activation of the TM catalyst, i.e., an electron transfer from the cathode to the metal complex, and subsequently a reduction of this signal caused by the interaction with the substrate.

The second application field will be the cathodic conversion of bis(alkoxycarbonyl) and bis(hydroxycarbonyl). Here it will be exploited that beside the charge state also ligand dissociation and exchange result in distinct changes in the absorption spectra of metal complexes. This should allow to follow the complete course of the reaction

Connection within the RTG. This PhD project will be jointly supervised by Stefan Lochbrunner and Robert Francke. After the setup is implemented, it will be applied to the systems studied in TP2 in close collaboration with the projects P2.1 and P2.2. The findings will be interpreted also based on the results of P2.3 and P2.4