



● timsTOF fleX as a new tool to discover electrochemical side reactions by laser desorption/ionization imaging

In the emerging fields of electroorganic synthesis and battery research, electrochemical side reactions on the active surface of electrodes represent a major challenge for efficiency and reproducibility.

Abstract

Often, the undesired polymerization of one or more compounds on the active surface of electrodes is observed. These polymers tend to adsorb on the electrode

leading to a passivation of the active surface, which is often referred to as "electrode fouling".

Mass spectrometric imaging using the timsTOF fleX enables the identification and the spatially

resolved visualization of the adsorbed side products. Hence, timsTOF fleX-based imaging allows the investigation of electrode fouling and provides valuable insight into electrochemical reaction pathways [1].

Keywords:
MALDI-MS imaging,
electrochemistry,
electrode fouling,
electrode surface
imaging, polymerization

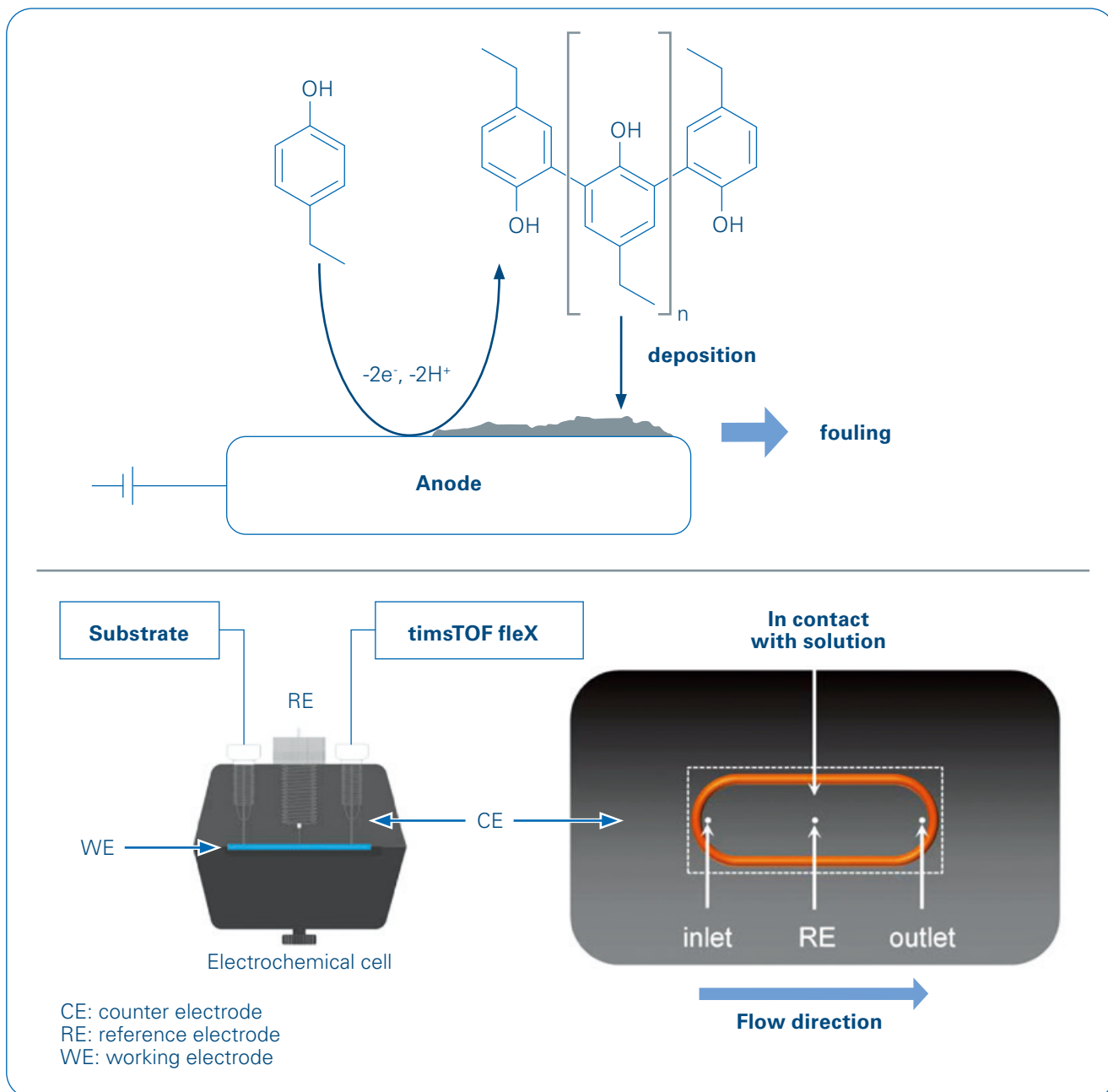


Figure 1. Top: Overview of the electrochemical polymerization of 4-ethylphenol to depict electrode fouling. Bottom: Setup of the electrochemical cell used for electrode fouling simulation.

Introduction

The recent renaissance of electrochemistry is due to different fields of application, including electroorganic synthesis [2,3] and modern battery research [4,5]. Hence, it is an important aspect of a sustainable usage of chemical resources and energy storage and can be considered

as part of green chemistry. A profound knowledge of the electrode's surface chemistry is necessary to control electrochemical conversions, typically initiated by single-electron-transfer reactions and followed by functionalization. Apart from the desired conversion, side reactions such as over-oxidation, homo-coupling or polymerization can take place and

need to be addressed to ensure high selectivity and efficiency [6]. Higher oligomers formed in this way may exceed their solubility limit and precipitate on the electrode surface. The resulting passivation of the electrode surface compromises the conversion efficiency and reproducibility. Therefore, it is commonly described as electrode fouling [7].

To better understand the surface processes, a detailed understanding of the surface chemistry is required and can be studied by high resolution mass spectrometric imaging. The necessity to analyze the electrochemical cell effluent as well as the manifold electrodes, varying in size and composition, requires high instrumental flexibility. The timsTOF fleX fulfills these demands with its dual ESI/MALDI source and the instrument feature such as the orthogonal qTOF setup. Therefore, the timsTOF fleX represents a powerful solution for materials imaging including studies of electrode surfaces.

Experimental

Two different reactions were studied in order to investigate electrode fouling and side-product formation pathways on their active surfaces. First, a polymerization of 4-ethylphenol, a classical building block chemical, was carried out in an electrochemical thin-layer flow-through cell under potentiostatic control as presented in Figure 1. The setup consisted of a boron-doped diamond (BDD) working electrode, used to investigate polymer formation. A 10 mM analyte solution in 10 mM ammonium formate buffer as electrolyte in water and acetonitrile (80:20, v/v, pH 9) was infused for one hour at a flow rate of $10 \mu\text{L min}^{-1}$. The applied oxidation potential of 2 V was previously optimized for highest conversion efficiency. Oligomers in the cell effluent were analyzed via direct injection ESI. After oxidation, the removable working electrode (30 x 12 x 1 mm) was rinsed with water and mounted on an ITO glass slide. As the oxidized compounds exhibit strong UV/vis absorbance, the electrode surface was analyzed by laser desorption/ionization (LDI) on the same timsTOF fleX platform in the negative ion mode. The lateral

resolution was set to $100 \mu\text{m}$ at a pixel acquisition rate of 10 Hz, resulting in a total measurement time of 1 h. The obtained imaging data was processed using SCiLS Lab (Bruker Daltonik).

Second, the method was transferred to studies of a dehydrogenative cross-coupling reaction, which is extensively described in literature [8-11]. To obtain the desired bisphenol

and to avoid over-oxidation products, it is necessary to maintain control over the oxidation steps at the BDD electrode surface [12]. In contrast to the above mentioned electrode, an in-house built adapter was required to fit the electrode dimensions ($70 \times 10 \times 3 \text{ mm}$) for LDI analysis. While maintaining the lateral resolution at $100 \mu\text{m}$, the pixel acquisition rate was adapted to 20 Hz, resulting again in a total measurement time of 1 h.

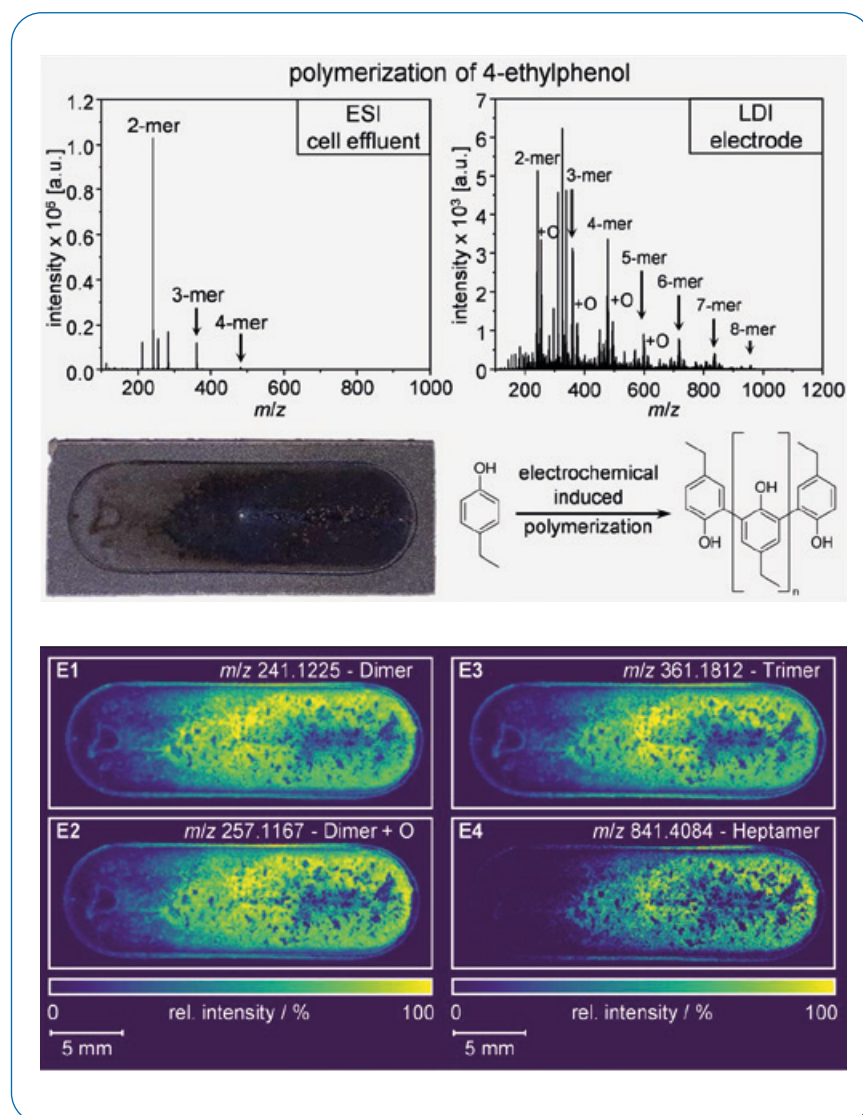


Figure 2. Top row: Comparison of the ESI mass spectrum of the cell effluent and the mean LDI mass spectrum of the BDD electrode after oxidation of 4-ethylphenol. Second Row: Photographic image of the electrode after electrochemical treatment and simplified polymerization scheme. Below: LDI-MS images (E1-E4) of the spatial oligomer distribution of oxidative polymerized 4-ethylphenol including one hydroxylated compound. The flow direction is from left to right.

Results and discussion

The oxidative electrochemically induced polymer formation of 4-ethylphenol was chosen to investigate electrode fouling in a flow-through cell experiment. As shown in Figure 2, the ESI mass spectrum of the cell effluent consists only of oligomer signals up to four monomeric units, whereas the LDI scanning of the electrode's surface enlightens the presence of adsorbed higher oligomers. In the latter case, monomeric species are suppressed by the selected ion transfer parameters of the mass spectrometer, while oligomeric species up to octamers were found to precipitate on the surface. These signal groups include hydroxylated species as well, and represent deprotonated and molecular anions. Figure 2 shows an optical image of the electrode exhibiting a strong darkening in flow direction (left to right) as well as the molecular distribution of selected oligomers. The spatial oligomer distribution correlates with the flow direction, while an area of lower abundance is observed in the center of the last third of the electrode. The overall adsorption pattern shows a perfect match with the darkening in the photograph. Therefore, it is concluded that precipitation leads to a conductive polymeric thin layer serving as condensation nuclei for the formation of new oligomers.

Moreover, this example shows the potential to deliver detailed lateral information on electrode side reactions allowing the optimization of reaction parameters and cell dimensions. Hence, the electrode surface of a targeted phenol-phenol cross-coupling from electroorganic synthesis was investigated as depicted in Figure 3. In the mean mass spectrum, signal groups from monomeric up to tetrameric species were

obtained. They consist of oligomers comprising different connectivity and over-oxidation functionalization such as hydroxylation, dehydrogenation and dealkylation. The formation of the desired cross-coupled product [AB]

(m/z 301.1440, [M-H]⁻) seems to happen predominantly in a comparably small area on the electrode, while the formation of the homo-coupled side product [AA] (m/z 305.1025, [M-H]⁻) is found over a larger area towards

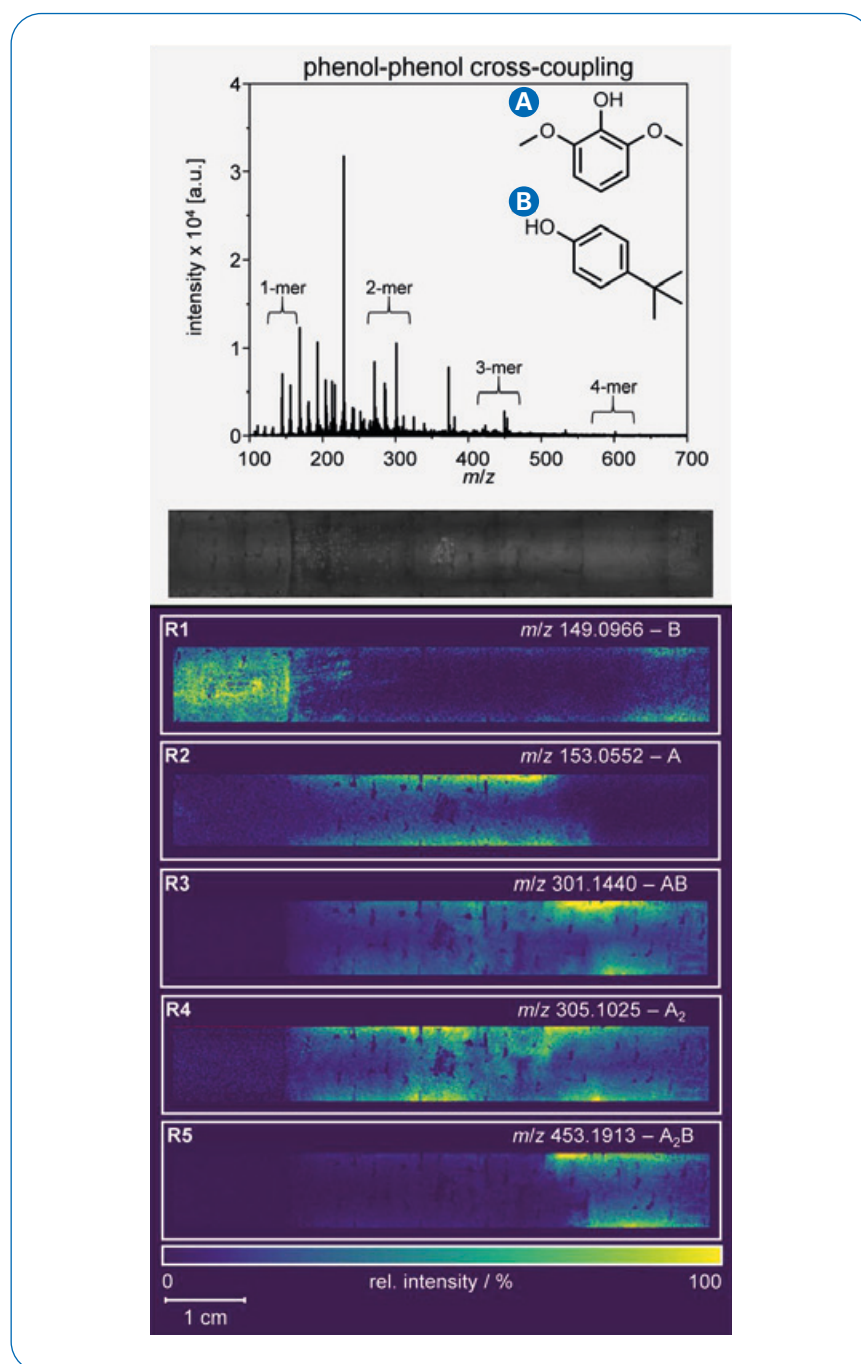


Figure 3. Top: Averaged LDI mass spectrum for the BDD electrode of the phenol-phenol cross-coupling reaction and optical image of the electrode after electrochemical treatment. Below: Selected LDI-MS images (R1-R5) of the monomer and oligomer distribution of oxidatively treated 2,6-dimethoxyphenol (A) and 4-(1,1-dimethylethyl)-phenol (B). The flow is from left to right.

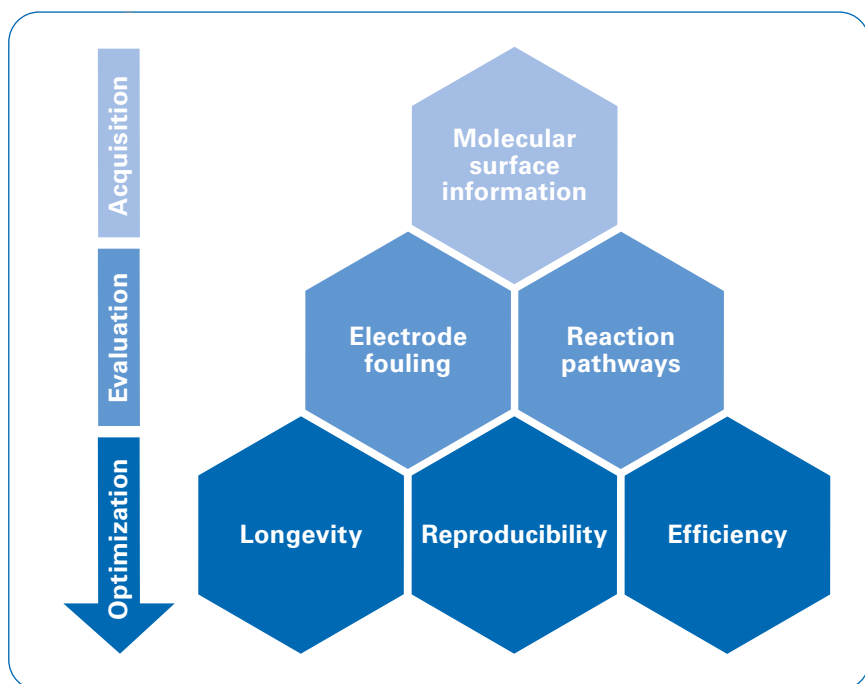


Figure 4. Information chain of electrode imaging by LDI-MS. The evaluation of the obtained molecular information allows to depict reaction pathways and unfavorable processes such as electrode fouling. This knowledge is a valuable factor for optimizing electrochemical processes regarding longevity, reproducibility and efficiency.

the electrode's center. The formation of higher oligomers based on these products can be depicted in the respective areas and needs to be addressed for optimum conversion efficiency.

Using the unique flexibility of the timsTOF fleX mass spectrometer to perform ESI and LDI experiments, it is possible to examine electrode fouling processes and reaction pathways at the molecular level. Therefore, timsTOF fleX is a powerful tool for an emerging field of modern research and industry.

Conclusion

- Bruker's timsTOF fleX delivers in-depth molecular information on electrochemical surface chemistry.
- The dual ESI/MALDI source provides information about dissolved and surface-adsorbed reaction products using one instrumental platform.
- The flexibility options of the timsTOF fleX allows the characterization of electrodes of varying surface texture, material and dimensions opening a wide range of applications in the field of material imaging.
- The high scan speed of the instrument allows to image the entire electrode surface within 1 h with a resolution of 100 μm .
- The obtained molecular information helps to understand surface processes allowing optimization of electrochemical processes.



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● **Bruker Daltonics GmbH & Co. KG** **Bruker Scientific LLC**

Bremen · Germany
Phone +49 (0)421-2205-0

Billerica, MA · USA
Phone +1 (978) 663-3660

ms.sales.bdal@bruker.com – www.bruker.com