Starter kit for electrochemical sensors based on polythiophene thin films – synthesis of films with improved properties and protocol for fast and gentle electrode regeneration

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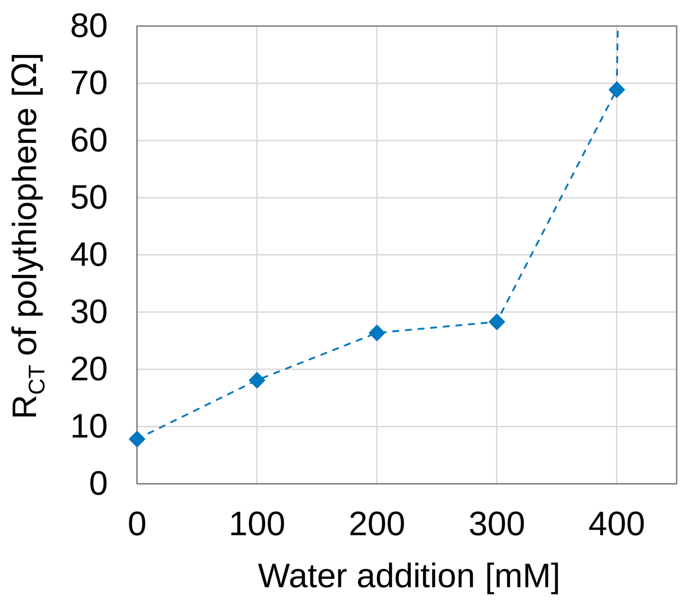
Motivation and Aim

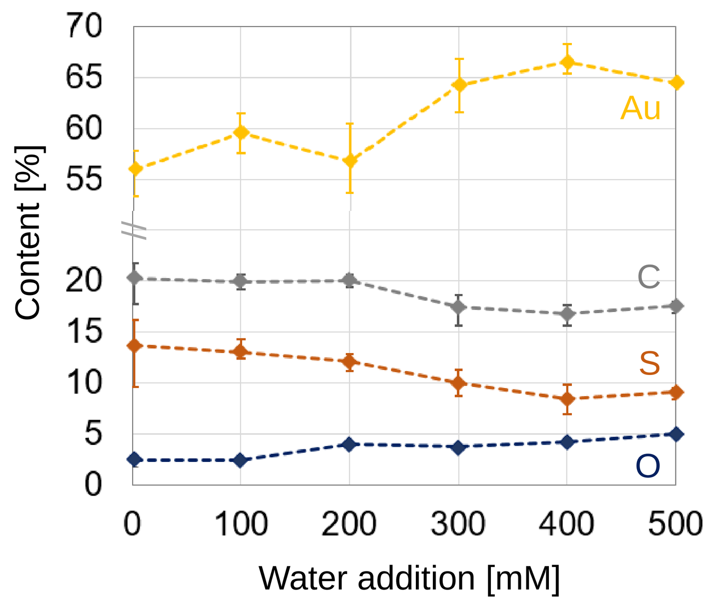
Due to their unique properties, polythiophene and other conductive polymers have become the subject of intensive research and are promising substrate materials for innovative and trendsetting applications. They convince with fast synthesis, great chemical and structural versatility, environmental stability, enhanced electron transfer, as well as reduced electron poisoning and fouling. To this day, boron trifluoride diethyl etherate [1] is the preferred solvent for electropolymerization of thiophene, although it does not allow for reproducible film qualities due to its decomposition under ambient conditions. Furthermore, due to their highyl stable absorption, the removal of conductive polymer films presents a challenging task and is oftentimes highlighted as a significant drawback in their utilization [2].

We therefore want to equip the reader with a starter kit for electropolymerization of high quality polythiophene films from stable solvents due the utilization of an appropriate catalyst to solvent drying and , as well as a simple, yet efficient method to remove the deposited films off the electrodes for their reuse.

Working solution drying

In order for the working solution to conduct electric current, supporting electrolytes in the form of hygroscopic salts have to be added. The presence of water, however, negatively affects electropolymerization of thiophene.

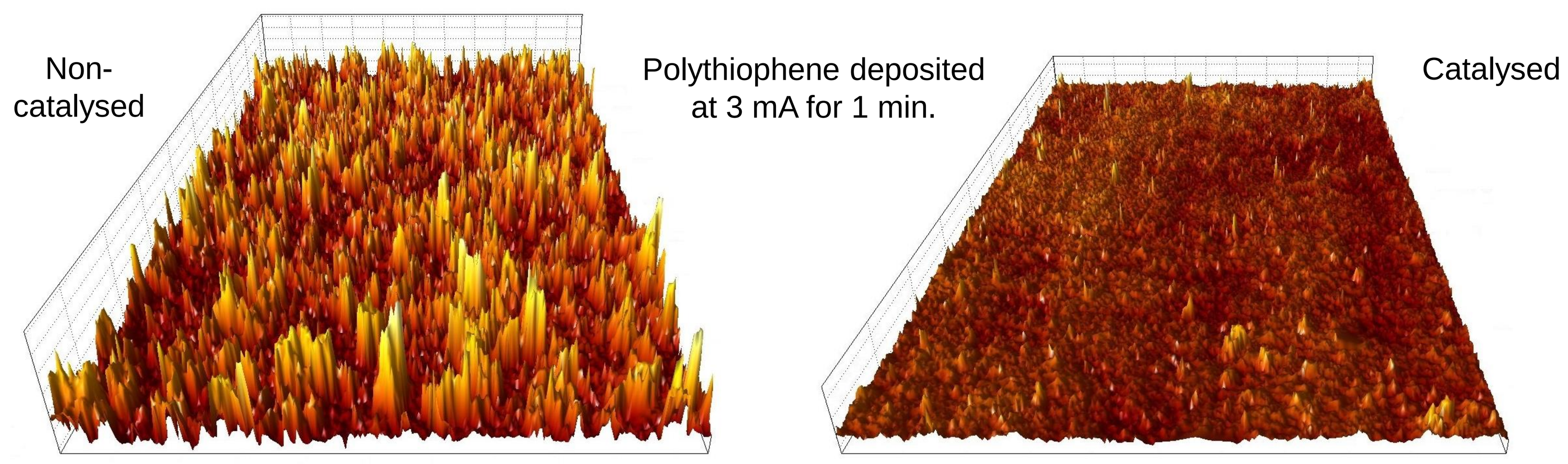




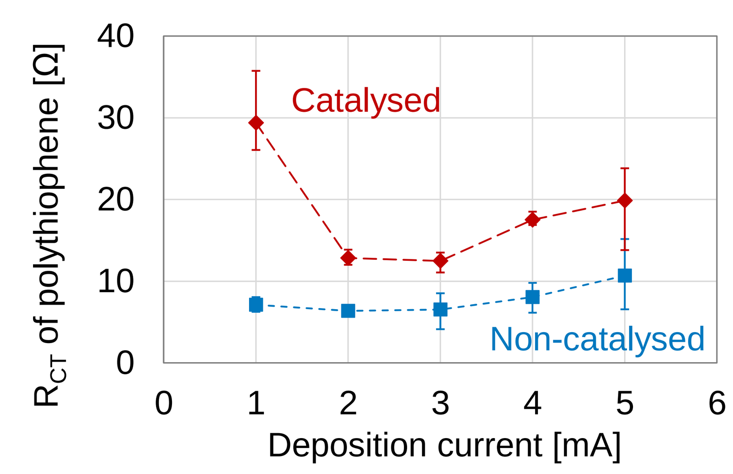
- The charge transfer resistance R_{CT}, which characterizes the conductivity perpendicular to the film, increases with increasing amounts of added water and completely inhibits electro-polymerization at concentrations ≥ 1 M added water.
- With increasing water content, the resulting films decrease in thickness and contain increasing amounts of oxygen, which points at the incorporation of carbonyl groups [3].
- ➢ We found that drying the working solution over molecular sieve consitutes a simple, yet effective method to remove water and allow for successful electropolymerization.

Lewis acid catalysis

We recently discovered that electropolymerization can be catalysed by Lewis acids, which facilitate monomer oxidation. We identified fluorine based Lewis acids as suitable class of catalysts, as they combine a high acidic strength with the necessary electrochemical stability. By exemplarily utilizing ZnF_2, we were able to synthesize polythiophene films from acetonitrile that constitute a promising substrate material for electrochemical biosensors.



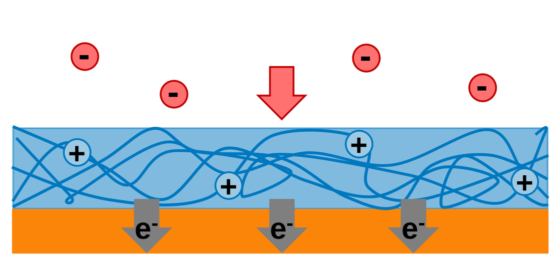
- Films were of significantly smoother surface topography, which minimizes sterical hindrance of subsequently immobilized bioreceptors and therefore should grant improved target binding.
- Films of reproducible and low charge transfer resistance R_{CT} could be obtained that enhance the electron transfer.



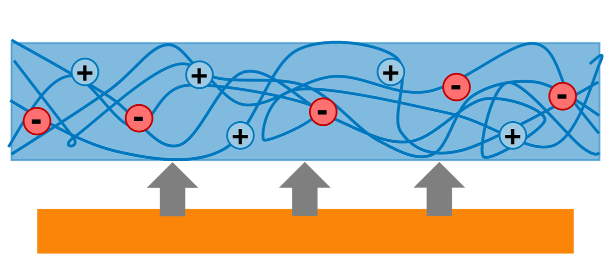
- ➢ By utilizing ZnF_2 as catalyst, films of high and reproducible quality can be obtained from dried working solutions.

Electrode regeneration

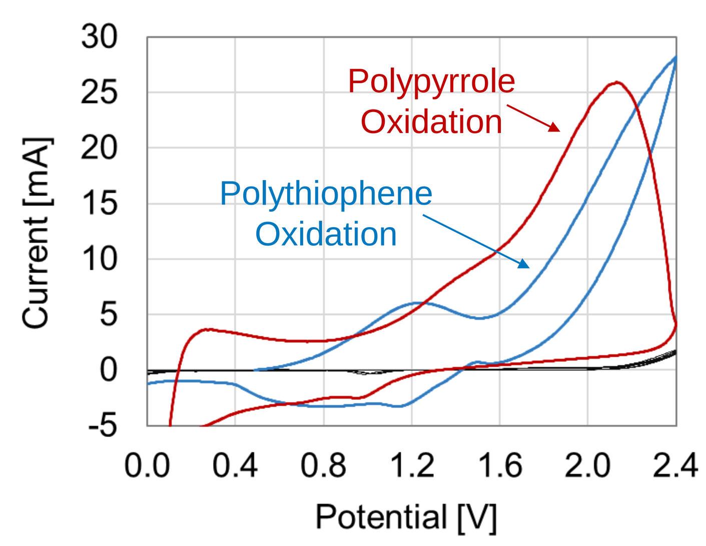
Our developed protocol [4] for polymer film removal alters the tension profile on the interphase polymer/gold to flake the films off the electrode. The polymer films are oxidized at high potentials, so that negatively charged counter ions diffuse into the film. The resulting film swelling introduces a shear stress to the interphase, which breaks the bonds that account for their highly stable absorption.

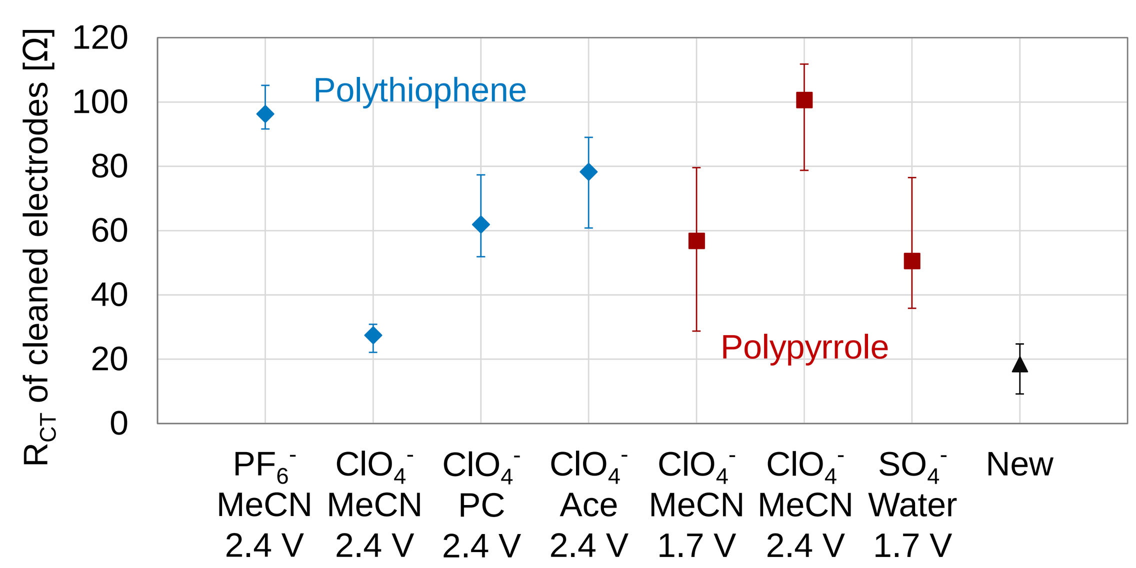


Film oxidation and ion diffusion



Delamination due to swelling





- Since the underlying principle of swelling is a universal process, a variety of solvents and counter ions can be employed for the removal of different conductive polymer films.
- ➢ Electrodes could be reused for up to fifteen times and allow for reproducible film qualities.

Conclusion and Outlook

- We found that the working solutions have to be water free to allow for efficient electropolymerization, which can effortlessly be achieved by storage over molecular sieve.
- Lewis acid catalysis allows for mild polymerization conditions and reproducible film synthesis. Fluorine based catalysts, such as AlF_3, TiF_4, ZnF_2, ZrF_4, InF_3, LaF_3, CeF_3, NdF_3 and GdF_3 represent ideal candidates, since they possess the required acidic strength and are electrochemically stable.
- The cleaning protocol is versatile and can be used with different solvents and counter ions to easily remove conductive polymer films and reuse the electrodes for upto fifteen times.

References

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[2] Bobade, R.S., *Journal of Polymer Engineering*, **2011**. 31(2-3).

[3] Roncali, J., et al., *Chem. Reviews*, **1992**. 92(4)

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