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Unravelling the catalysis of thiophene electropolymerization for improved film properties in a reproducible manner – turning our backs on boron trifluoride diethyl etherate[†]

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Abstract: Polythiophene and other conductive polymers can be electropolymerized from a number of solvents, of which boron trifluoride diethyl etherate (BFEE) is preferably used. In this solvent, electropolymerization can be carried out under significantly milder conditions than in alternative solvents, which grants the polymer films superior mechanical and electrical properties. However, research published on this topic neither reports on the irreproducibility of film quality, nor the reason for the milder conditions in BFEE. In this communication, we unravel the catalysing effect of BFEE and identify Lewis acids on fluorine basis as suitable catalysts that enable the synthesis of polythiophene films from alternative solvents in a reproducible manner.

Keywords: Conductive polymers, polythiophene, electropolymerization, BFEE, Lewis acid catalysis

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1. Introduction

Since *nomen est omen*, conductive polymers are most famous for their ability to conduct electric current, making them an interesting substrate material for a number of applications, such as polymer-based transistors, actuators, light-emitting diodes, electrochromic devices, electrochemical capacitors, and electrochemical sensors [1]. In order to be conductive, the polymers have to be transferred from a neutral to a charged state, which is referred to as doping. Doping and de-doping are reversible processes and do not degrade the polymer backbone. However, if a high potential is applied, conductive polymers undergo irreversible over-oxidation, which causes rapid structural degradation and loss of electro-activity.

Polymerization and doping can both be performed by electrochemical methods, that polymerize, deposit, and dope the polymers in one step. For the electropolymerization of thiophene, a variety of solvents was utilized that include acetonitrile, benzonitrile, nitrobenzene, propylene carbonate, dimethyl sulphate, diethyl sulphate, and dichloromethane [2-5]. In these solvents, a relatively high potential of ≥1.6 V has to be applied to initiate polymerization. Unfortunately, at this potential, polythiophene already over-oxidizes. This issue was suitably termed as "polythiophene paradox" [3].

Remedy provides the solvent boron trifluoride diethyl etherate (BFEE), in which thiophene already oxidizes at 1.0 V [6]. Due to the milder polymerization conditions, polythiophene films synthesized in BFEE are of improved mechanical and electrical properties. Therefore, BFEE seems to be the ideal solvent for electropolymerization of polythiophene and other polymers, which is why it was predominantly used in the past 20 years. However, published research on this topic is shy to report on the reproducibility of film synthesis. We found that polythiophene film quality varies greatly, when deposited in BFEE, which we will discuss in detail in the first half of this communication.

The question now arises, why BFEE grants milder polymerization conditions and how the underlying mechanism could be transferred to stable solvents. This way, high-quality polythiophene films could be synthesized in a reproducible manner. In this communication, we unravel the catalytic effect of BFEE on thiophene oxidation. We identified Lewis acids on fluorine basis as suitable catalysts, as they combine strong acidity with electrochemical stability. By exemplarily utilizing zinc fluoride, we were able to decrease the initial oxidation potential in acetonitrile and polymerized polythiophene films in a reproducible manner.

2. Materials and Methods

3.1. Electrodes and equipment

Screen-printed thick film electrode chips (SPE) with integrated gold working electrode, silver reference electrode and platinum counter electrode (model DRP-250AT) were obtained from Metrohm DropSens (Llanera, Spain). For electropolymerization, the integrated silver electrode was used. For characterization, an external Ag/AgCl reference electrode (Sensortechnik Meinsberg, Xylem Analytics Germany, Germany) was used. Electrochemical procedures were performed using the SP-300 potentiostat/galvanostat with impedance analyser (Bio-Logic Science Instruments SAS, Claix, France).

Electrochemical procedures were performed using the SP-300 potentiostat/galvanostat with impedance analyser (Bio-Logic Science Instruments SAS, Claix, France). Impedance measurement was deducted with a sinusoidal 7.07 mV rms excitation voltage around the DC potential of 0 V in the frequency range from 100 kHz to 10 Hz. The measurement buffer contained potassium ferricyanide and potassium ferrocyanide, 2 mM each. Impedance spectra were fitted with the Randles-Ershler equivalent circuit [7, 8] with a constant phase element instead of a capacitor.

3.2. Electrode cleaning

We recently reported on the development of a simple, yet gentle protocol for the removal of conductive polymers from gold electrodes [9]. The coated electrodes were incubated in 2 M sodium perchlorate in acetonitrile, and a constant potential of 2.4 V was applied for one minute. The films were removed by rinsing or wiping with a Q-tip. Subsequently, the silver reference electrodes were regenerated by treatment with a Q-tip that was immersed in 30 mg/ml aqueous thiourea until the shiny silver surface was restored.

3.3. Electropolymerisation

Cyclic voltammetry was deducted from 0 – 2 V, starting from the open circuit potential, with a scan rate of 20 mV/s in a variety of working solutions. Electropolymerization was also performed by chronopotentiometry under the conditions mentioned in the text.

If BFEE was employed as solvent, handling was performed under argon. After the experiments, the working solution was pipetted into a saturated solution of sodium bicarbonate to quench boron trifluoride [10].

3. Results and Discussion

3.1. Investigation of thiophene electropolymerisation in BFEE

We intend to deposit a high-quality polythiophene film onto gold electrodes as the first step in the construction of an impedimetric biosensor. Due to its conductive character, the film mediates the electron transfer between the working electrode and the redox mediator utilized in impedance spectroscopy. The conductivity perpendicular to the film can thereby be estimated by the charge transfer resistance R_{CT}. Films with R_{CT} lower than the R_{CT} of cleaned electrodes (20 – 35 Ω) enhance electron transfer and are therefore beneficial for the analytic performance of the biosensor.

We electropolymerized 50 mM thiophene in BFEE at potentials ranging from 1.1 – 1.3 V for 0.5 – 2 minutes and found that the lowest R_{CT} of 120.3 Ω could be obtained by electropolymerization at 1.2 V for 1 minute. This value could not be reproduced, if newly made working solutions were utilized, as can be seen from Table 1. However, if the same working solution was employed, a good reproducibility with a deviation of 8.3% was achieved.

Table 1. Electropolymerization of 50 mM thiophene in BFEE at 1.2 V for 1 minute. Films were characterized by electrochemical impedance measurement. Obtained values of charge transfer resistance R_{CT} [Ω] are listed in this table.

Individual working solutions	**Same working solution**	**Individual working solutions with 100 mM DMP**	**Individual working solutions with 1 M water**[1]
120.3 Ω	222.5 Ω	71.2 Ω	16.2 Ω
175.4 Ω	199.5 Ω	173.2 Ω	74.8 Ω
222.5 Ω	189.4 Ω	627.7 Ω	52.8 Ω

[1] Electropolymerization at 1.1 V for 1 minute

BFEE is hygroscopic and absorbs moisture from the air, which is why we carefully handled it under argon. Under the influence of water, oxygen, and UV light, BFEE is known to decompose to diethyl etherate and boron trifluoride (see Figure 1 a). The latter forms a number of hydrates that eventually disintegrate to form the ionic species $[BF_3OH]^-$ [11]. It is thought to serve as supporting electrolyte and counter ion during electropolymerization [12]. Furthermore, free hydrogen ions are generated, that are known to initiate a thiophene additive reaction [13]. From this, thiophene trimers result, whose central unit is hydrogenated (see Figure 1 b). The incorporation of such trimer would disrupt the conjugated system of the polymer and therefore decrease its conductivity.

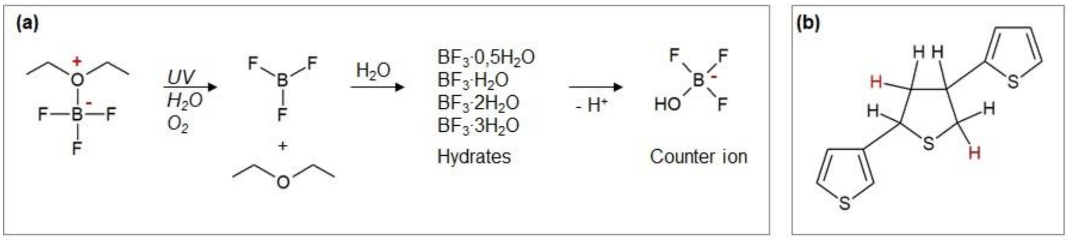

Figure 1. Schematic representation of (a) BFEE decomposition and (b) thiophene trimer with hydrogenated central unit.

To prevent the formation of such trimers, so-called proton scavengers can be utilized that complex with free hydrogen ions. For this purpose, trialkylaluminium compounds and sterically hindered amines are oftentimes used. By using di-*tert*-butylpyridine (DTBP), Jin et al. [14] could increase the conductivity of free standing polythiophene films from 100 S/cm to 1300 S/cm. We decided to purchase 2,6-dimethyl pyridine (DMP) due to its dramatically lower cost and higher basicity, compared to DTBP, which should increase the affinity of the proton scavenger to complex with free hydrogen ions.

Since DMP is hygroscopic, we aliquoted it under argon and prepared our working solution consisting of 50 mM thiophene in BFEE with differing concentrations of DMP. Besides fresh BFEE that was taken from the original bottle, we also used previously aliquoted BFEE that had changed its colour to brown. Polythiophene films were again synthesized at 1.2 V for 1 minute. The obtained R_{CT} demonstrated that with the addition of 75 – 100 mM DMP, polythiophene films could easily be synthesized from fresh and old BFEE in a reproducible manner. However, when using the same DMP aliquot to create new working solutions, the R_{CT} increased significantly with each new batch (see Table 1). We ascribe this to the hygroscopic nature of DMP. Therefore, handling in a glove box seems to be necessary, which is, however, quite impractical.

We generally encountered that the current during electropolymerization in BFEE was quite low (<1 mA) and wondered if a higher conductivity of the working solution would have a positive effect on reproducibility. Since solubility of salts in BFEE is extremely low, we decided to add water to the working solution to trigger the formation of $[BF_3OH]^-$. The measured current during polymerization indeed increased to values even exceeding 2 mA. The lowest R_{CT} was achieved by deposition at 1.1 V for 1 minute with the addition of 1 M water. With 16.2 Ω, it was even lower than the R_{CT} of the uncoated electrode. The repeat, however, again demonstrated irreproducible results (see Table 1).

It would therefore be crucial to understand why BFEE grands significantly milder polymerization conditions and how the underlying mechanism could be transferred to stable solvents. This way, high-quality polythiophene films could be synthesized with ease in a reproducible manner.

3.2 Unravelling the catalytic effect of Lewis acids during electropolymerization

While investigating the effect of water on thiophene electropolymerization in BFEE, we found that the initial oxidation of thiophene was shifted to lower potentials. As can be seen from Figure 2 a, in pure BFEE, the initial oxidation potential was 1.13 V and could be decreased to a potential as low as 0.84 V by the addition of 1 M water. A similar decrease could be observed by Xu et al., who added 5% v/v of sulphuric acid [15] or trifluoroacetic acid [16] to BFEE. Such additives partially decompose BFEE and therefore increase the concentration of boron trifluoride, which is known as a strong Lewis acid. Shi et al. [6], who were the first to employ BFEE for thiophene electropolymerization, hypothesized that BFEE catalyses the *deprotonation* of thiophene, which has apparently not been questioned ever since. Deprotonation constitutes the third step in the mechanism of electropolymerization of thiophene (see Figure 2 b). During deprotonation, two hydrogen atoms are abstracted from a charged dimer, which is previously formed by coupling of two cation radical species. These radicals result from the first step of electropolymerization, the oxidation of uncharged monomers, which takes place *at the initial oxidation potential*.

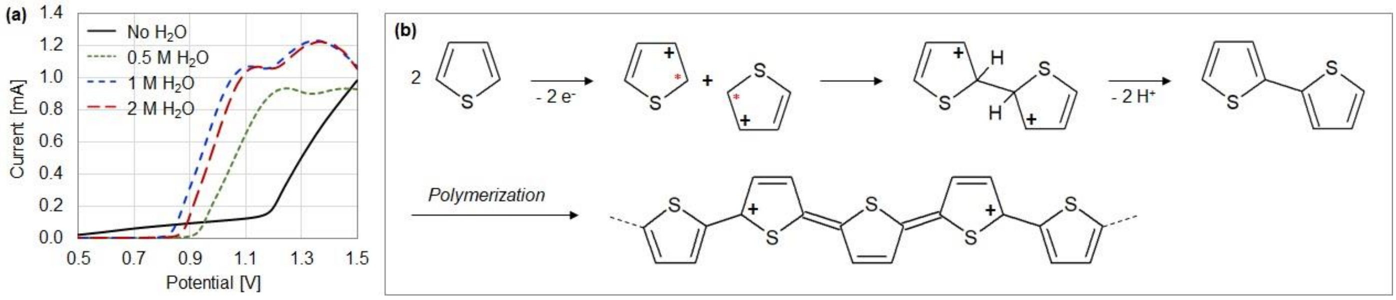

Figure 2. Electropolymerization of thiophene: (a) polarization curves of 100 mM thiophene in BFEE with the addition of water; (b) schematic representation of electropolymerization mechanism. The p-type doped polymer contains the doubly charged Bipolaron.

Why should catalysing deprotonation in the third step have an effect on the initial oxidation potential that is determined in the first step? Lewis acids possess an empty molecular orbital and act as electrophiles. Therefore, it would stand to reason that they facilitate the abstraction of an electron from the monomers during oxidation. To test this hypothesis, we employed $AlCl_3$, a common Lewis acid catalyst, to investigate its effect on the electropolymerization of thiophene in acetonitrile. The obtained voltammograms are picture in Figure 3 a. Without the Lewis acid, thiophene oxidizes at potentials >1.7 V, while in the presence of 2 M $AlCl_3$, a broad peak with two maxima was observed at lower potentials. The negative control of $AlCl_3$ revealed that it was not stable in the investigated potential window and decomposed at potentials >0.9 V. The second peak is thought to correspond to thiophene oxidation *at significantly lower potentials*.

With the help of the catalyst it was now possible to synthesize a film at 1.4 V. Raman spectroscopy of the deposit showed the distinctive peaks of C=C stretching vibrations and

C-S-C ring deformation, as can be seen in Figure 3 b. Therefore, our hypothesis of Lewis acid catalysis for thiophene polymerization at low potentials can be confirmed as true.

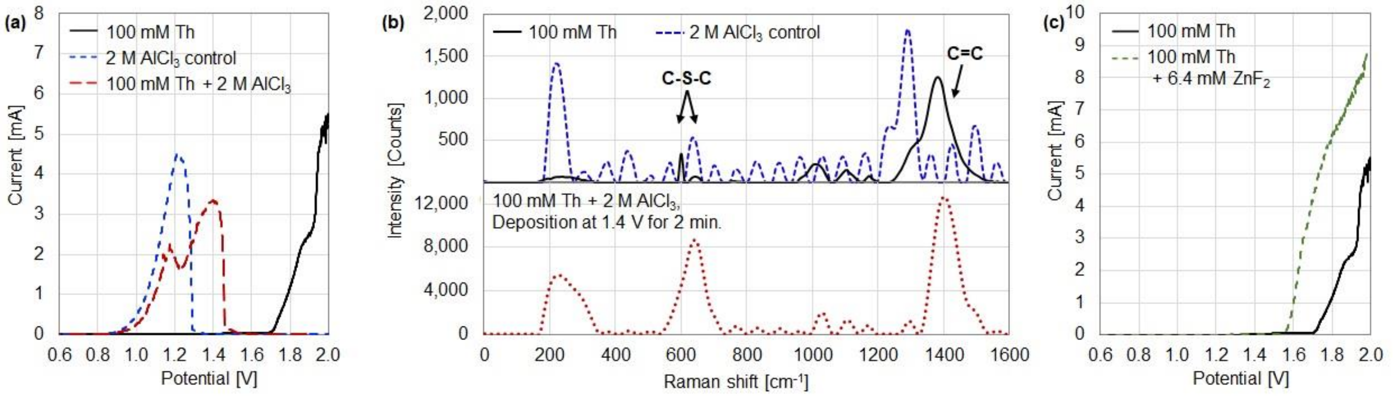

Figure 3. Electropolymerization of thiophene under the influence of (a) $AlCl_3$ and (c) ZnF_2. All CV scans were performed in acetonitrile with 100 mM KPF_6 as supporting electrolyte/counter ion. (b) Raman spectrum of a film deposited at 1.4 V catalyzed by 2 M $AlCl_3$ in comparison to the spectra of the deposit from the $AlCl_3$ control and polythiophene.

Electrochemical stability therefore represents a limiting factor for the choice of an appropriate catalyst. According to the electrochemical series, the only halide based Lewis acids that are stable in the potential window are fluorides. We identified the following acids as promising candidates, as they are not gaseous, not highly hazardous and not prone to hydrolysis: AlF_3, $TiAl_4$, ZnF_2, ZrF_4, InF_3, LaF_3, CeF_3, NdF_3 and GdF_3. We chose to purchase ZnF_2 to investigate its effect on thiophene electropolymerization.

The saturation solubility of ZnF_2 in acetonitrile was measured to be 6.4 mM (± 9%). When thiophene was polymerized via CV from a saturated solution of ZnF_2, the initial oxidation potential could be decreased from 1.70 V to 1.55 V, as can be seen from Figure 3 B. Compared to $AlCl_3$, the effect of ZnF_2 on the initial oxidation potential is not as major, which is probably due to its low solubility. However, the experiments prove the successful application of fluorine based Lewis acids as catalyst for thiophene electropolymerization.

By utilizing ZnF_2, it is possible to deposit polythiophene films at 1.5 V, which was not possible without the catalyst. Three films were synthesized and could be characterized by a mean R_{CT} of 29.7 Ω (± 6.4%). At 1.6 V, films resulted with a mean R_{CT} of 25.1 Ω (± 15.5%), which was even lower than the R_{CT} of uncoated electrodes. Films deposited at 1.6 V for 1 minute without ZnF_2 had a mean R_{CT} of 57.3 Ω (± 20.4%).

4. Conclusion and Outlook

In this report, we unravel the mechanism behind the oftentimes-reported decreased initial oxidation potential of thiophene in BFEE. Low oxidation potentials prevent overoxidation and side reactions. As a result, films of desirably high conductivity can be obtained. However, BFEE undergoes a series of decomposition reactions under ambient conditions, so that film qualities cannot easily be reproduced.

We found that, due to its Lewis-acidic character, BFEE catalyses the oxidation of thiophene, which is the reason for the observed decrease of the initial oxidation potential. This discovery paves the way to catalyse electropolymerization in solvents that do not decompose, and therefore allows for high quality polythiophene films that can be synthesized in a reproducible manner. We identified Lewis acids on fluorine basis as suitable catalysts, as they possess the required acidic strength and electrochemical stability.

In addition to polythiophene, BFEE is used for the electropolymerization of a variety of other conductive polymers to similarly enable their mild synthesis. There seems to be a considerable need for our newly found catalysis, as the electropolymerization of benzene [17], carbazole [18], phenanthrene [19], thianaphtene [20], naphthalene [21], and indole [22] has been performed in BFEE under the addition of various Brønsted acids to further decrease the initial oxidation potential. Their electropolymerization could additionally benefit from the utilization of a fluorine based Lewis acid in stable solvents, as it enables reproducible film qualities.

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