

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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Motivation and Aim

Conductive polymers are most famous for their ability to conduct electric current, making them an interesting substrate material for polymer-based transistors, actuators, light-emitting diodes, electrochromic devices, electrochemical capacitors, and electrochemical sensors [1]. The conductivity of such polymers arises from the movement of charge carriers along the polymer backbone, which are created by reductive or oxidative doping. Polymerization and doping can both conveniently be performed by electrochemical methods in a single step. However, the applied potential must not be too high, since the polymers will undergo over-oxidation that causes rapid structural degradation and loss of electro-activity. Multiple solvents are available for thiophene electropolymerization, which are accompanied by individual advantages and, however, considerable drawbacks:

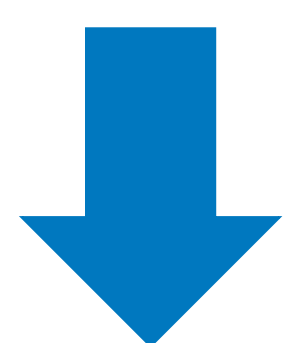
Boron trifluoride diethyl etherate (BFEE):

- ✓ Mild polymerization conditions
- ✓ Low initial polymerization potential: 1.0 V [2]
- ✓ Superior mechanical and electrical film properties
- ✗ Lack of transparency in literature regarding irreproducible results

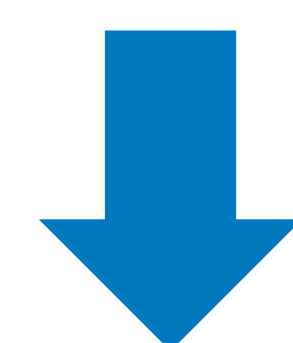


Acetonitrile, benzonitrile, nitrobenzene, propylene carbonate, dimethyl sulphate, diethyl sulphate, and dichloromethane [3-6]:

- ✓ Wide selection of stable solvents
- ✗ High initial polymerization potential: ≥ 1.6 V [3]
- ✗ Over-oxidation leads to low film quality



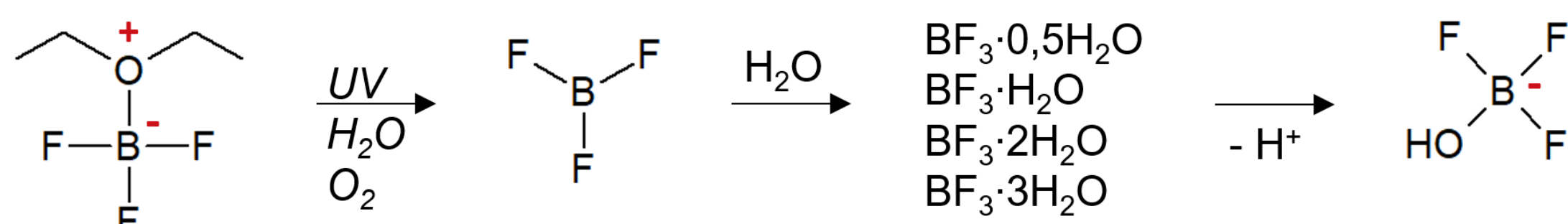
Why does BFEE grant milder polymerization conditions?
How can the underlying mechanism be utilized to allow the synthesis of high-quality polythiophene films from stable solvents in a reproducible manner?



Problem: Irreproducible polymerization

Utilization of BFEE as solvent

- BFEE grants mild polymerization conditions and therefore was predominately used in the past 20 years
- However, it undergoes a series of decomposition reactions:

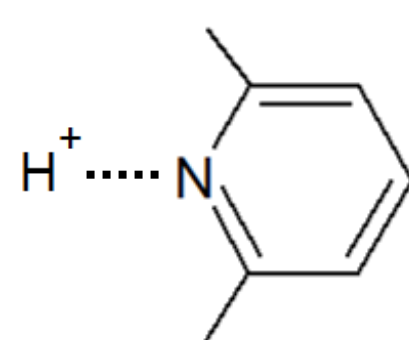


- Unlike films from the same working solution, films from different working solutions show a large deviation of their charge transfer resistance R_{CT} , which characterizes the conductivity perpendicular to the film

R_{CT} of films from 50 mM thiophene deposited at 1.2 V for 1 min.	In BFEE without additives	BFEE with DMP
Same working solution	203.8 Ω \pm 8.3%	76.6 Ω \pm 3.9%
Different working solutions	172.7 Ω \pm 29.6%	292.2 Ω \pm 100.8%

Addition of a proton scavenger

- 2,6-dimethyl pyridine (DMP) was employed to complex free hydrogen ions that derive from BFEE decomposition
- With each new working solution, the R_{CT} increased, which we ascribe to the hygroscopic nature of DMP
- Handling BFEE or DMP under argon alone does not inhibit water absorption/decomposition. Working in a glove box seems to be necessary to achieve reproducible results, which is however quite impractical.



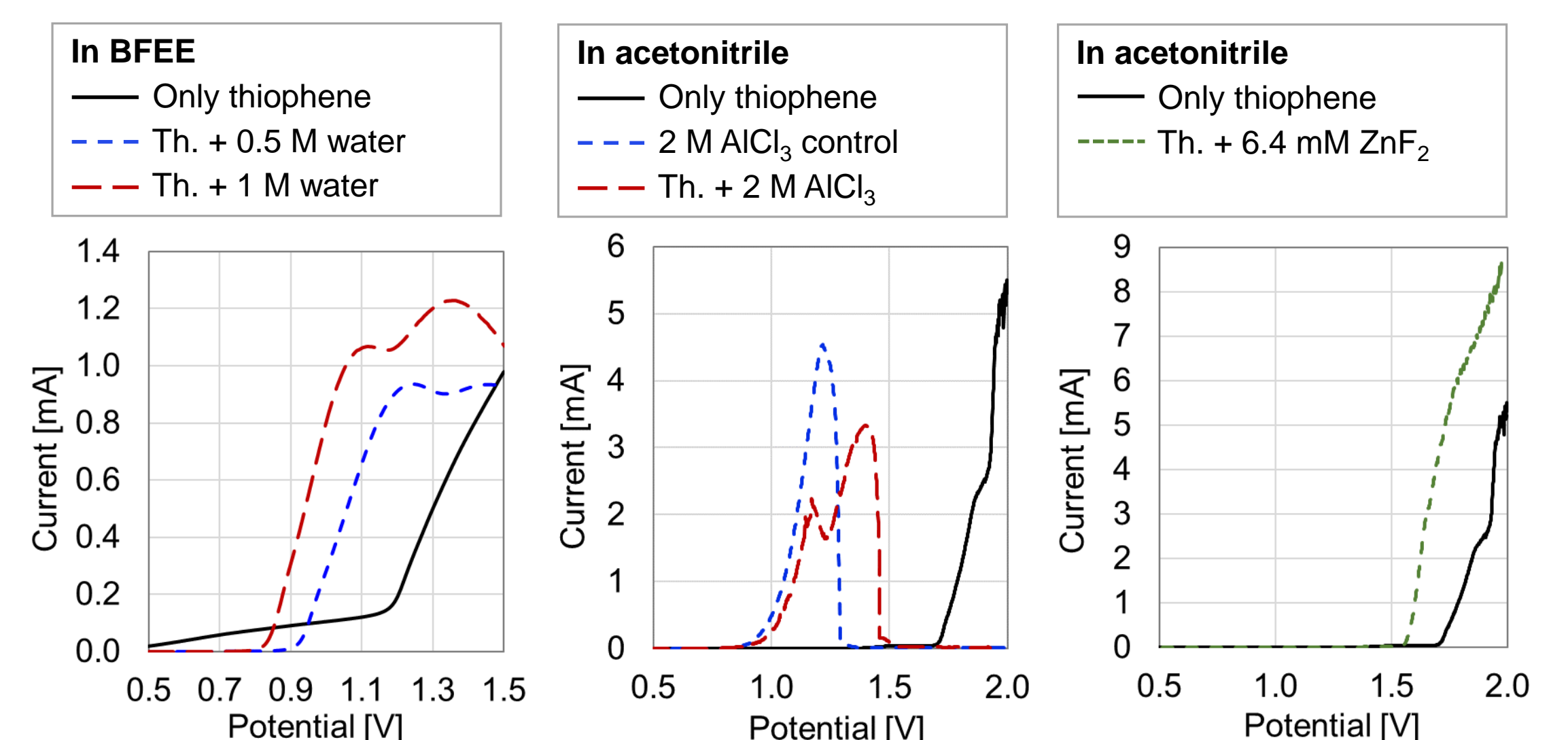
Conclusion and Outlook

- To grant mild polymerization conditions for conductive polymer films with superior properties, we found that catalysation in stable solvents can be performed
- We identified Lewis acids on fluorine basis as appropriate catalysts, as they are electrochemically stable and of strong acidity
- We successfully used ZnF_2 for electropolymerization in acetonitrile. Due to its low solubility (6.4 mM), its effect on the initial oxidation potential was not as major as of the instable $AlCl_3$
- Promising alternatives could be: AlF_3 , $TiAl_4$, ZrF_4 , InF_3 , LaF_3 , CeF_3 , NdF_3 , and GdF_3 as they are not gaseous, not highly hazardous, and not prone to hydrolysis

Solution: Catalysation in stable solvents

Discovery of catalysation

- When adding water to the BFEE working solution, a decreased initial polymerization potential could be observed
- We hypothesized that the Lewis acidic character of BF_3 catalyses the oxidation of thiophene monomers during electropolymerization
- For confirmation, we polymerized thiophene in acetonitrile with $AlCl_3$, a common Lewis acid catalyst, and found a significant decrease of the initial oxidation potential



Appropriate catalyst

- $AlCl_3$ was found to be instable at potentials > 0.9 V
- Of the halide based Lewis acids, only fluorides are stable and therefore represent promising candidates
- Organometallic compounds are also stable, but not acidic enough, since the organic ligands shield the acidic metal centre
- Exemplarily, ZnF_2 was utilized and found to be stable and of strong acidity to successfully catalyse thiophene oxidation
- Due to its low solubility (6.4 mM), the effect of ZnF_2 on the initial oxidation potential was not as major as of the instable $AlCl_3$

References

- [1] Le, T.H., et al., *Polymers*, 2017. 9(4)
- [2] Shi, G., et al., *Science*, 1995. 267(5200)
- [3] Roncali, J., et al., *Chem. Rev.*, 1992. 92(4)
- [4] Aeiyaich, S., et al., *J. Electroanal. Chem.*, 1997. 434(1-2)
- [5] Sato, M.-a., et al., *Synthetic Metals*, 1986. 14(4)
- [6] Hotta, S., et al., *Synthetic Metals*, 1983. 6