

## Electronic Supplementary Information available

“Ionic conductivity enhancement in solid polymer electrolytes by electrochemical *in situ* formation of an interpenetrating network”

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By

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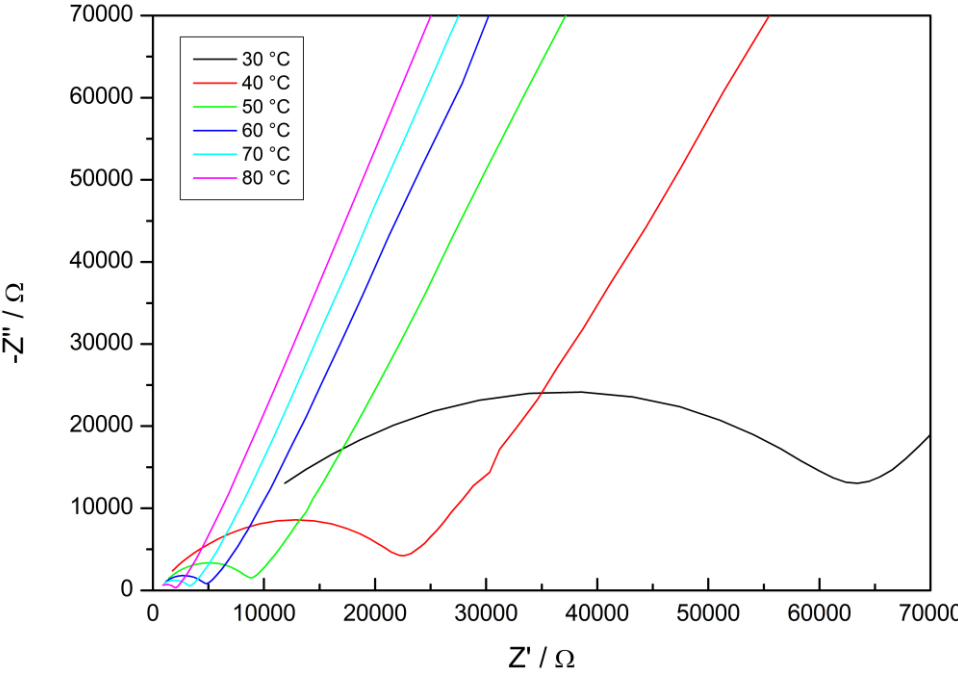
## Table of Contents

- S1. Impedance profiles of a) SPE, b) I-SPE-oPPy, c) I-SPE-oPMePy and d) I-SPE-oPEDOT at different temperatures.
- S2. Arrhenius plot of a) SPE and b) I-SPE-oPPy before (non-humid) and after storage in a humid environment for 24 hours and impedance profiles of c) SPE (humid) and d) I-SPE-oPPy (humid).
- S3. Electrochemical synthesis and overoxidation of PPy on glassy carbon electrode as example.
- S4. a) Oxidation and overoxidation of PPy and b) determination of the degree of overoxidation.
- S5. Study of the electroactivity of modified oPPy/GC electrode by cyclic voltammetry, using a) the negatively charged redox marker  $[\text{Fe}(\text{CN})_6]^{4-}$  and b) the positively charged redox marker  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  in relation to c) the non-overoxidized PPy.
- S6. References

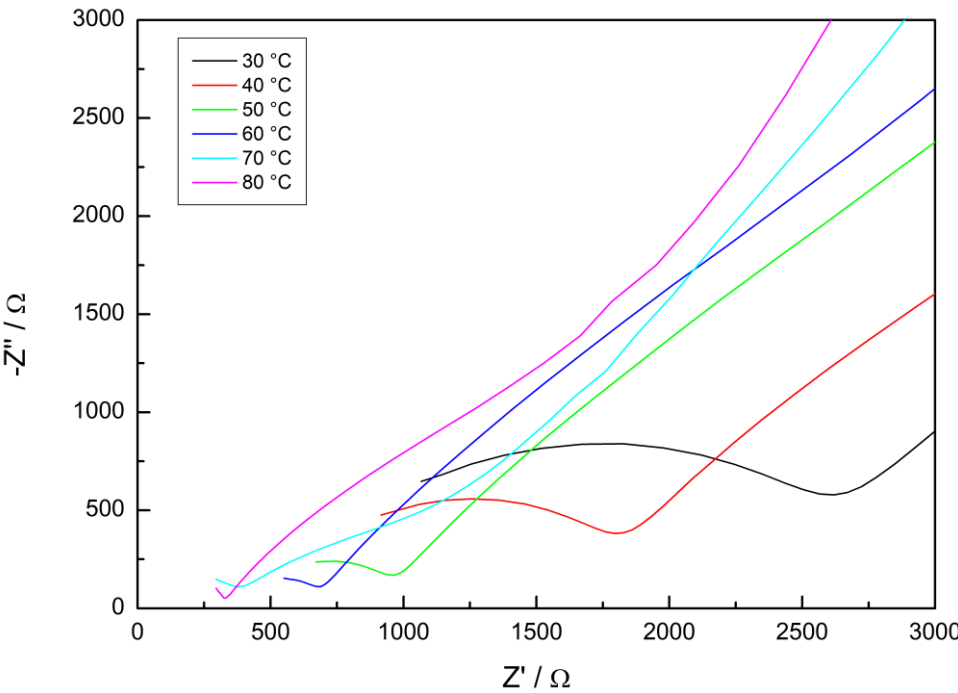
**S1. Impedance profiles of a) SPE, b) I-SPE-oPPy, c) I-SPE-oPMePy and d) I-SPE-oPEDOT at different temperatures.**

The electrochemical impedance spectroscopy measurements were performed within a frequency range of  $10^6$  Hz to 1 Hz with an AC amplitude of 20 mV. Equivalent circuit for SPE: [R(RQ)Q]. Equivalent circuit for I-SPEs: [R(RQ)(RQ)Q], with  $R$  = resistance and  $Q$  = constant phase element.

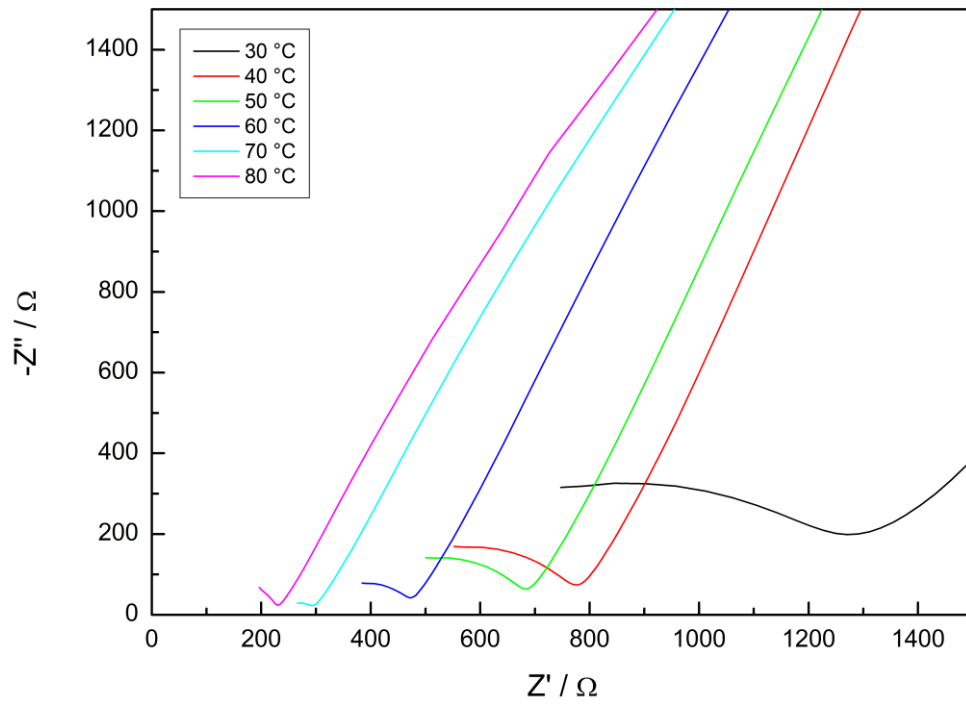
**a)**



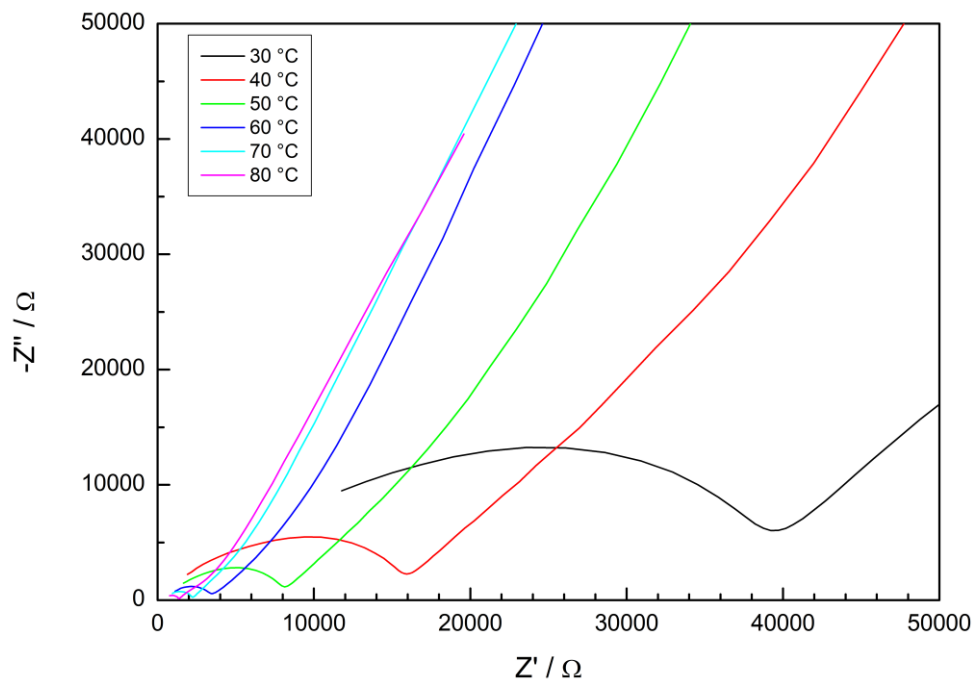
**b)**



c)



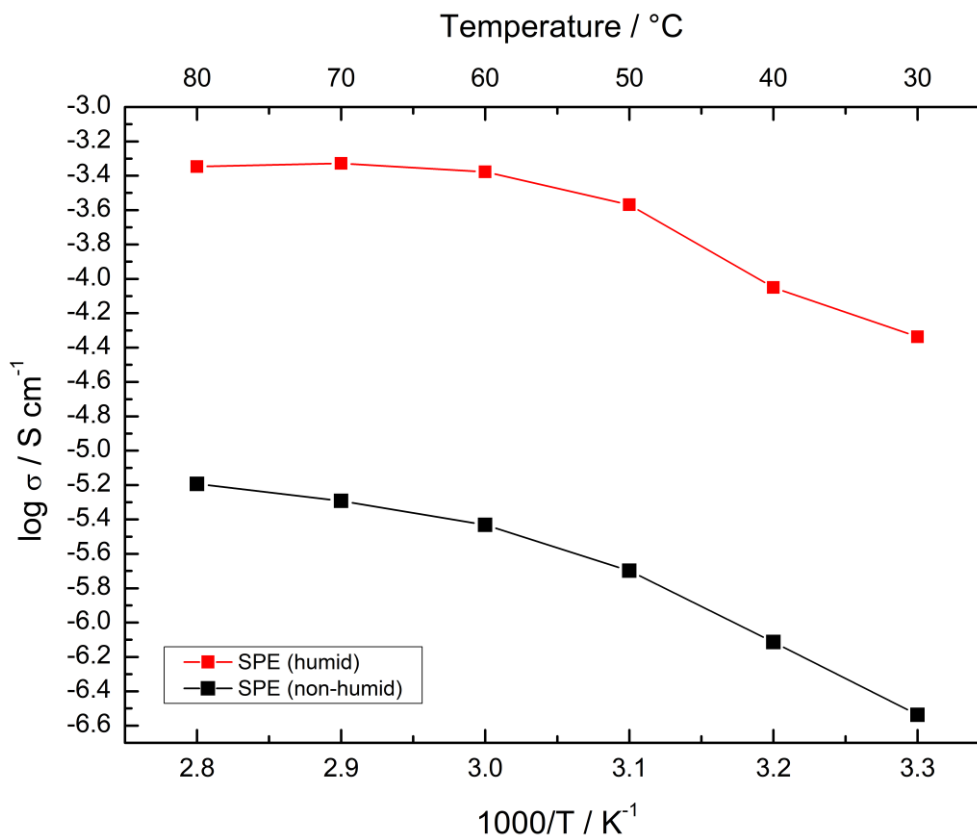
d)



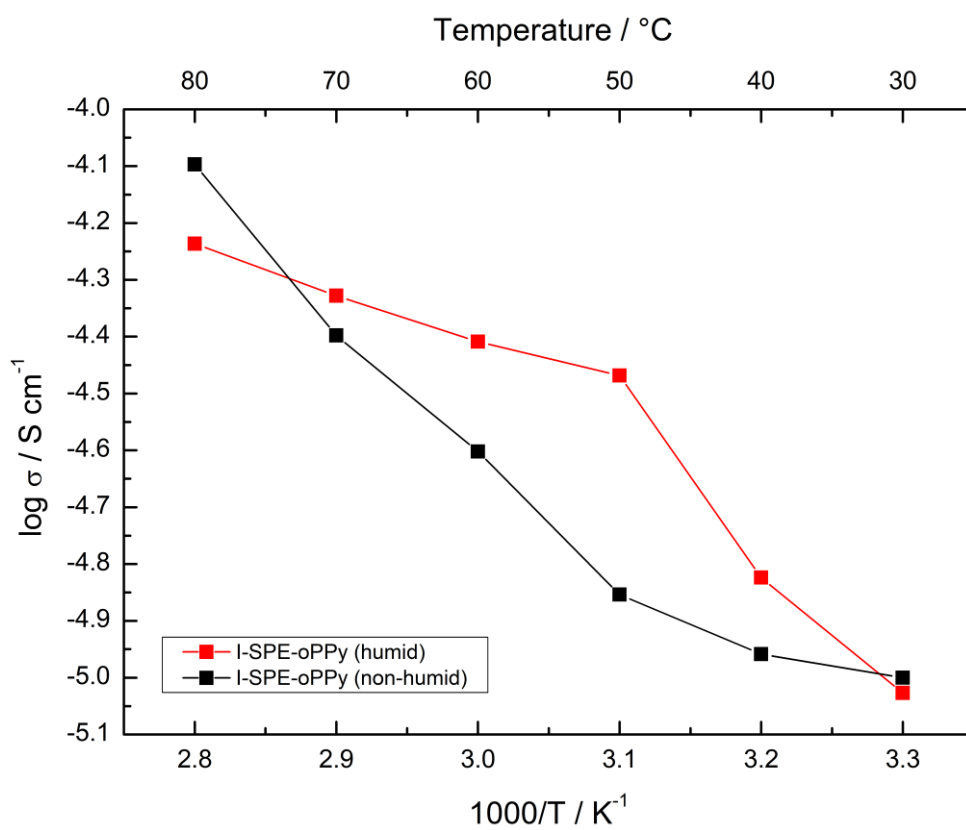
**S2. Arrhenius plot of a) SPE and b) I-SPE-oPPy before (non-humid) and after storage in a humid environment for 24 hours and impedance profiles of c) SPE (humid) and d) I-SPE-oPPy (humid).**

The electrochemical impedance spectroscopy measurements were performed within a frequency range of  $10^6$  Hz to 1 Hz with an AC amplitude of 20 mV. Equivalent circuit for SPE: [R(RQ)Q] at low temperature and [LR(QR)] at higher temperatures. Equivalent circuit for I-SPE-oPPy: [R(RQ)Q], with  $R$  = resistor,  $Q$  = constant phase element and  $L$  = inductor.

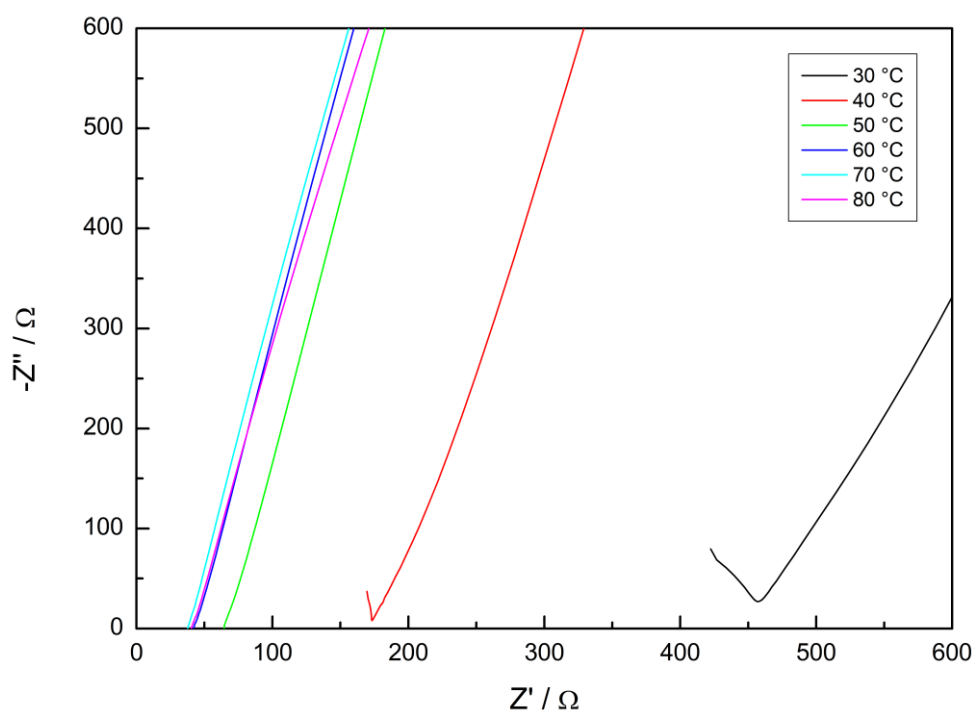
**a)**



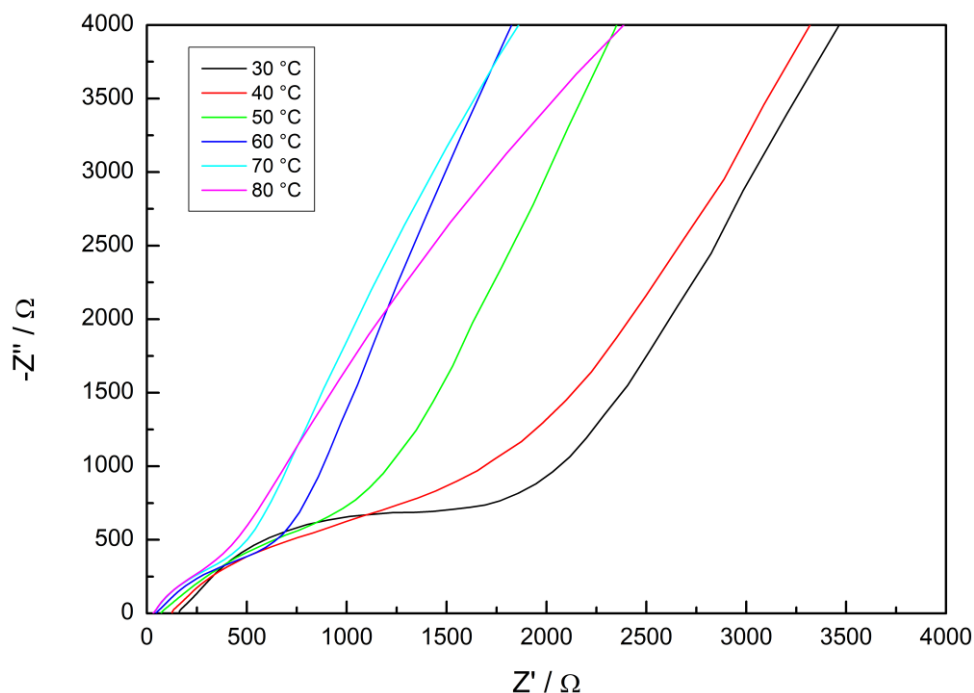
b)



c)

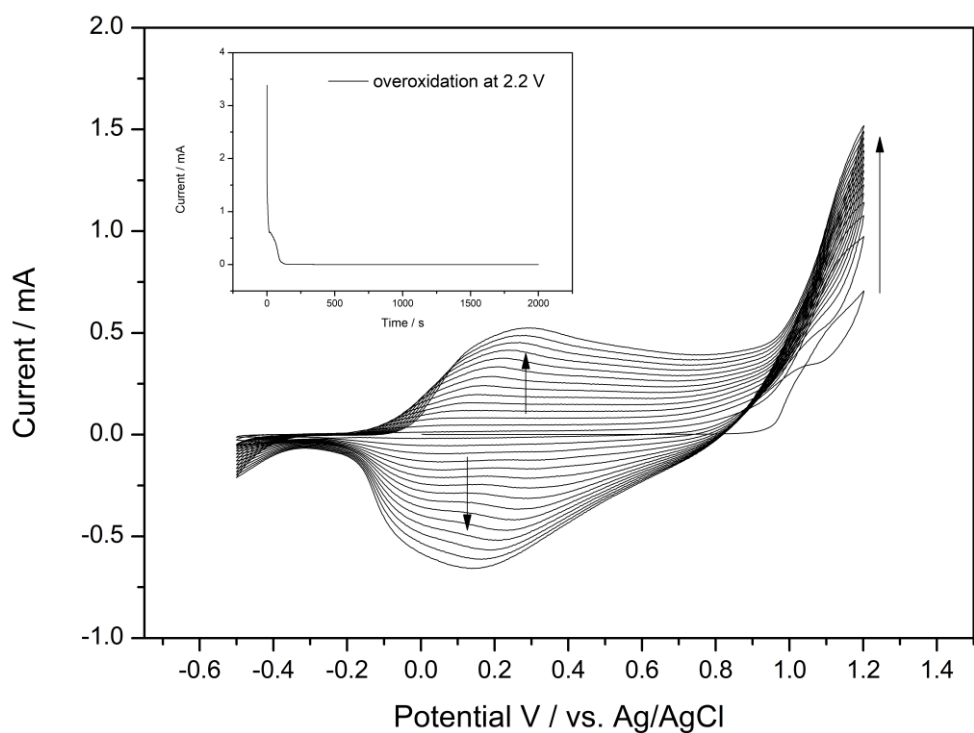


d)



### S3. Electrochemical synthesis and overoxidation of PPy on glassy carbon electrode as example.

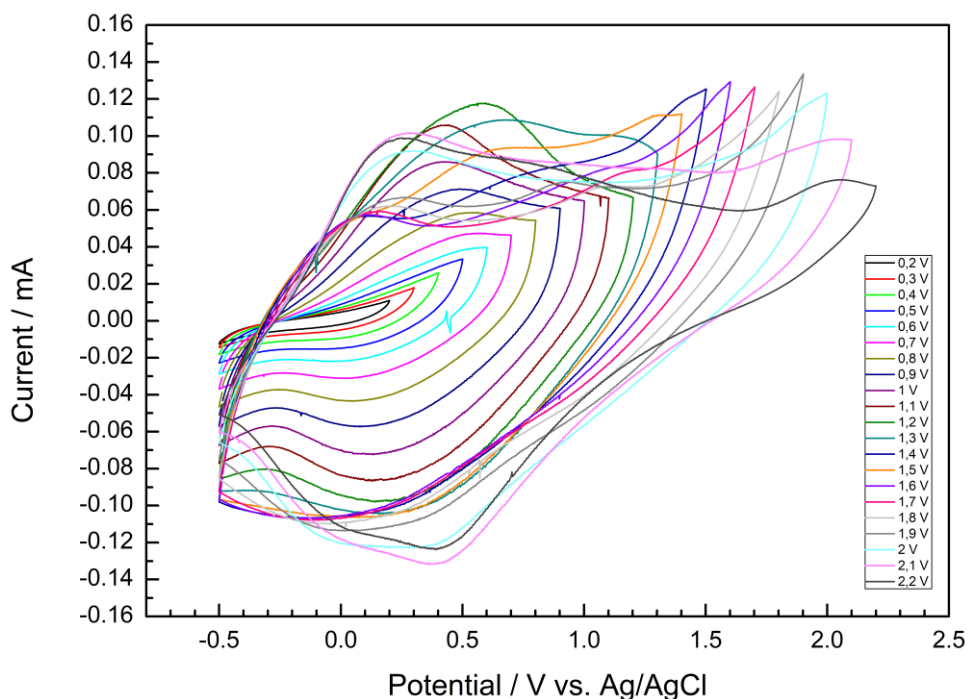
The electrodeposition was performed in a three-electrode setup with glassy carbon as working electrode, a platinum-sheet counter electrode and Ag/AgCl as reference electrode. The electrolyte was composed of 0.2 M LiTFSI and 0.1 M pyrrole in acetonitrile. The measurement was performed with a scan rate of 100 mV/s between -0.5 and 1.2 V for 15 cycles. The overoxidation was performed in an electrolyte composed of 0.2 M LiTFSI in acetonitrile at a constant potential of 2.2 V for 2000 s.



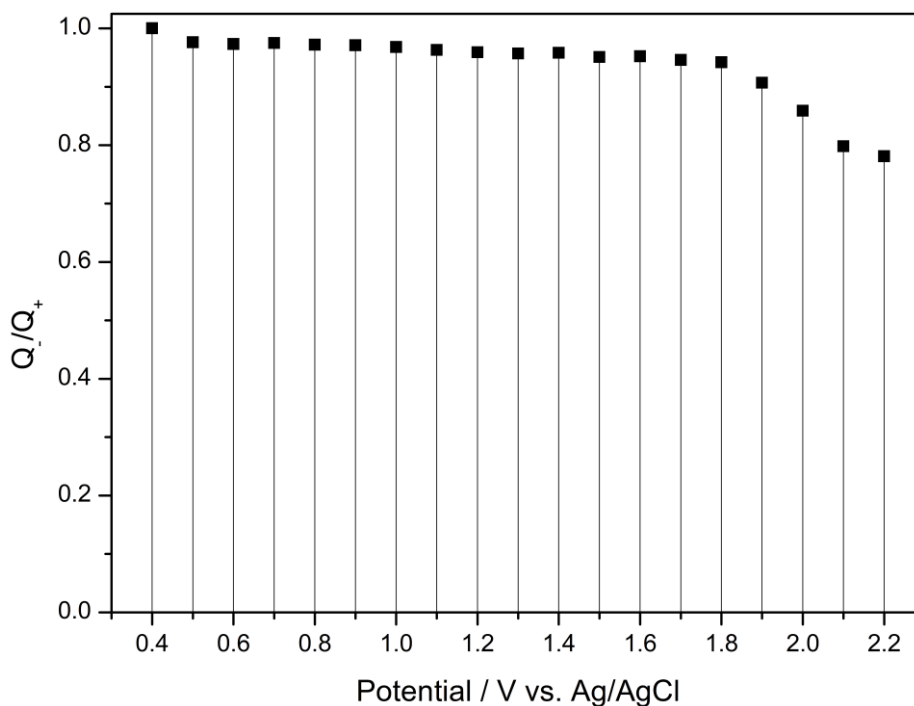
**S4. a) Oxidation and overoxidation of PPy and b) determination of the degree of overoxidation.**

The degree of oxidation of the deposited PPy on the GC electrode was examined in a monomer-free electrolyte solution of 0.2 M LiTFSI in acetonitrile at different potentials with a platinum-sheet counter electrode and a Ag/AgCl reference electrode. The charge ratio ( $Q_-/Q_+$ ) at each potential was calculated by division of the integral areas of positive and negative charge. A value of 1 indicates oxidation, whereas a value smaller than 1 indicates increasing overoxidation.<sup>1</sup>

**a)**



**b)**

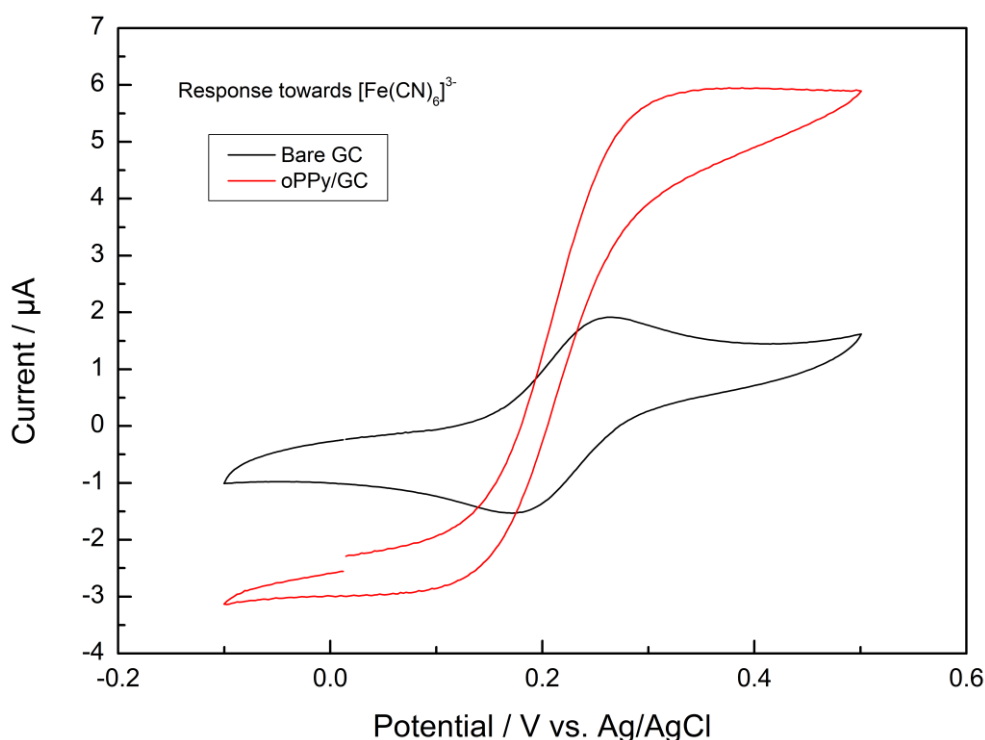




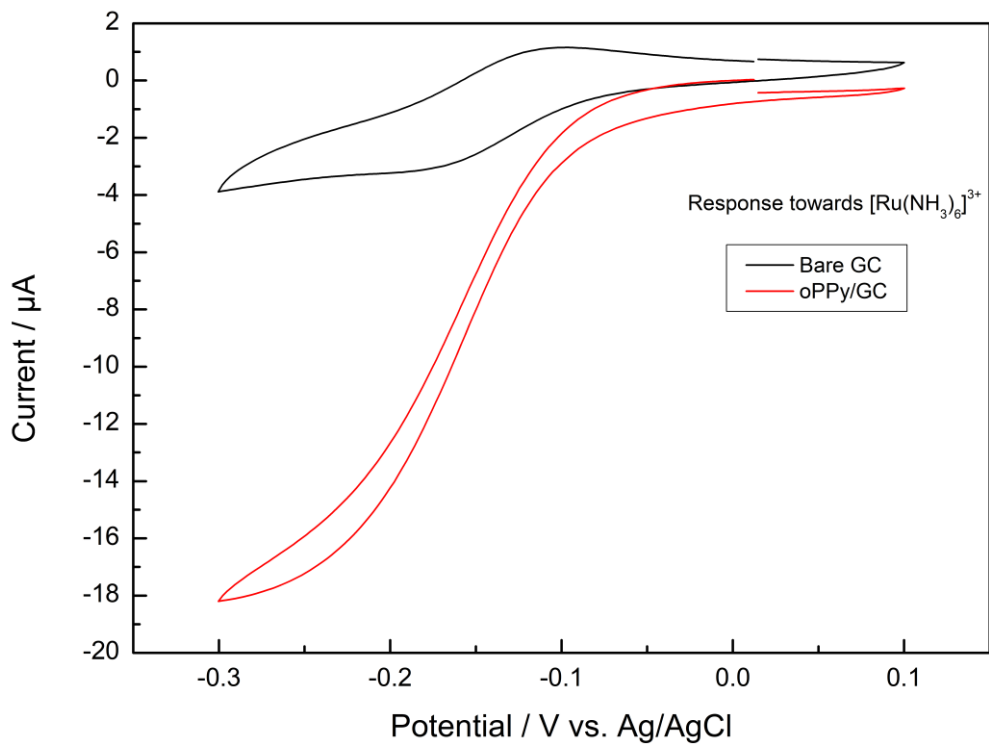
**S5. Study of the electroactivity of modified oPPy/GC electrode by cyclic voltammetry, using a) the negatively charged redox marker  $[\text{Fe}(\text{CN})_6]^{4-}$  and b) the positively charged redox marker  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  in relation to c) the non-overoxidized PPy.**

The electroactivity of overoxidized PPy on a glassy carbon electrode was examined.<sup>2</sup> First, the oPPy was deposited on glassy carbon according to the procedure from S3. The oPPy/GC electrode was then immersed and examined in different aqueous electrolyte solutions composed of a) 1 mM  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and 0.1 M KCl and b) 1 mM  $\text{Cl}_3[\text{Ru}(\text{NH}_3)_6]$  and 0.1 M KCl. A cyclic voltammogram was recorded (platinum-sheet counter electrode and Ag/AgCl as reference electrode) at a scan rate of 10 mV/s between -0.1 and 0.5 V. In relation to the overoxidized PPy, a cyclic voltammogram was recorded between -0.5 and 0.5 V at a scan rate of 50 mV/s with non-overoxidized PPy (c).

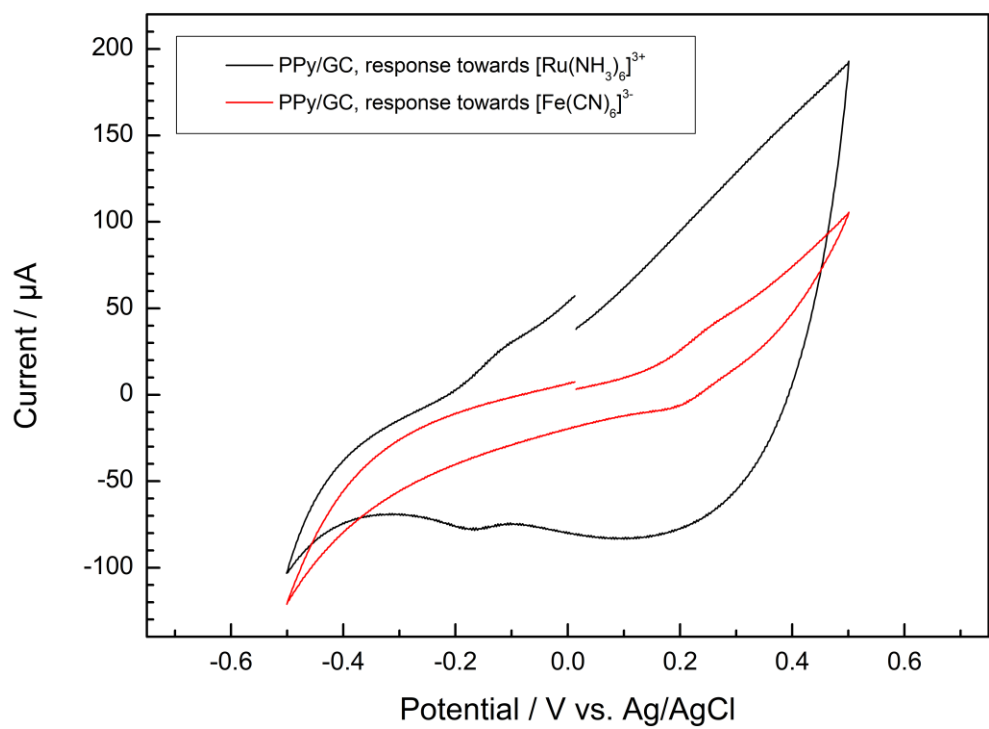
**a)**



**b)**



**c)**



## S6. References

- 1 M. Skompska, M. A. Vorotyntsev, M. Refczynska, J. Goux, E. Lesniewska, G. Boni, C. Moise, *Electrochim. Acta.*, 2006, **51**, 2108-2119.
- 2 S. Mondal and M. V. Sangaranarayanan, *Phys. Chem. Chem. Phys.*, 2016, **18**, 30705-30720.