

Supplementary Information for: Enhancing the conductivity of plasma polymer functionalized electrodes using gold nanoparticles

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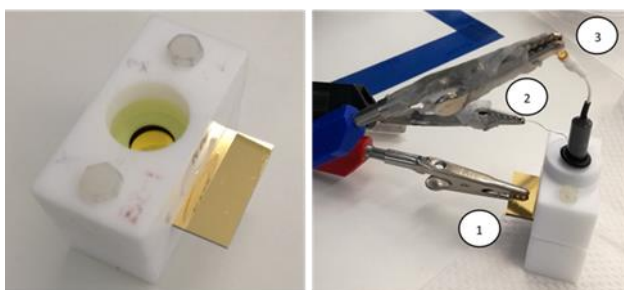


Figure S11: Image of the working electrode (1) assembled in an electrochemical cell and the counter (2) and working (3) electrodes connected to the cell.

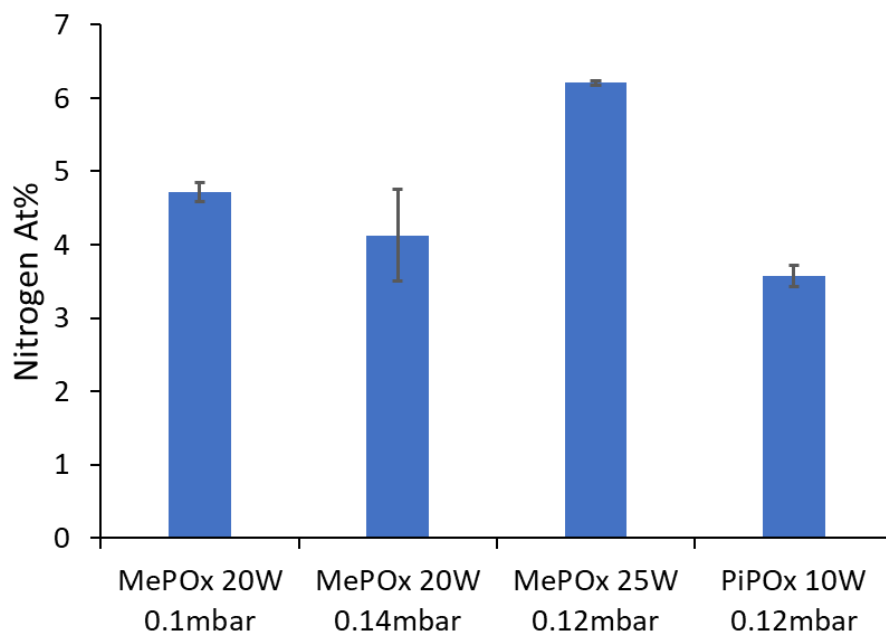


Figure S12: Atomic percentage of Nitrogen detected from thin MePOx and PiPOx films.

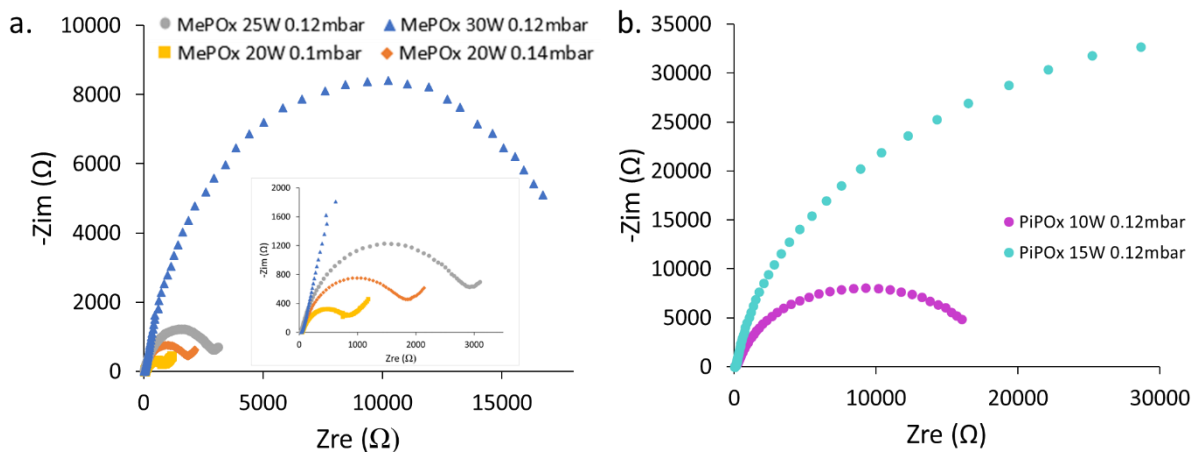
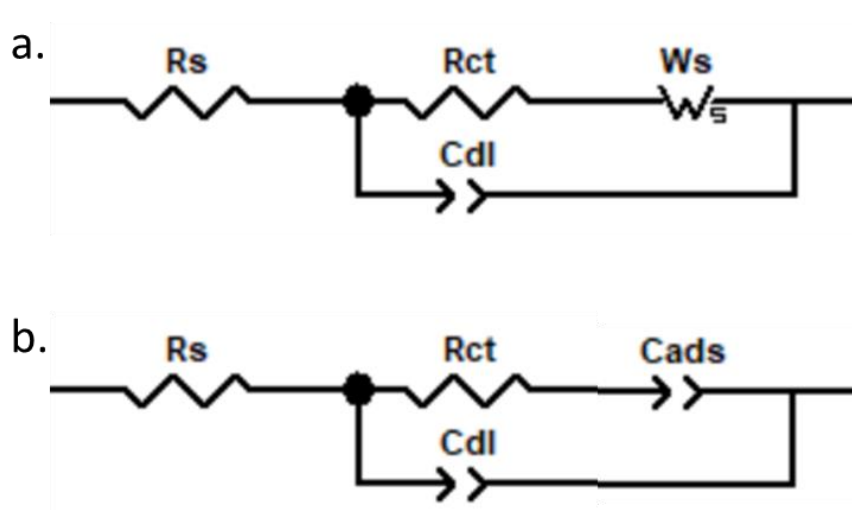


Figure S13: Representative Nyquist plots of a) MePOx films and b) PiPOx films.



R_s : Resistance of solution
 R_{ct} : Charge transfer resistance
 W_s : Warburg element
 C_{dl} : Double layer capacitance
 C_{ads} : Capacitance of adsorbed species

Figure S14: a) Equivalent circuit used to fit EIS measurement data in bulk electrochemical measurements. b) Equivalent circuit used to fit EIS measurement data in surface bound electrochemical measurements.

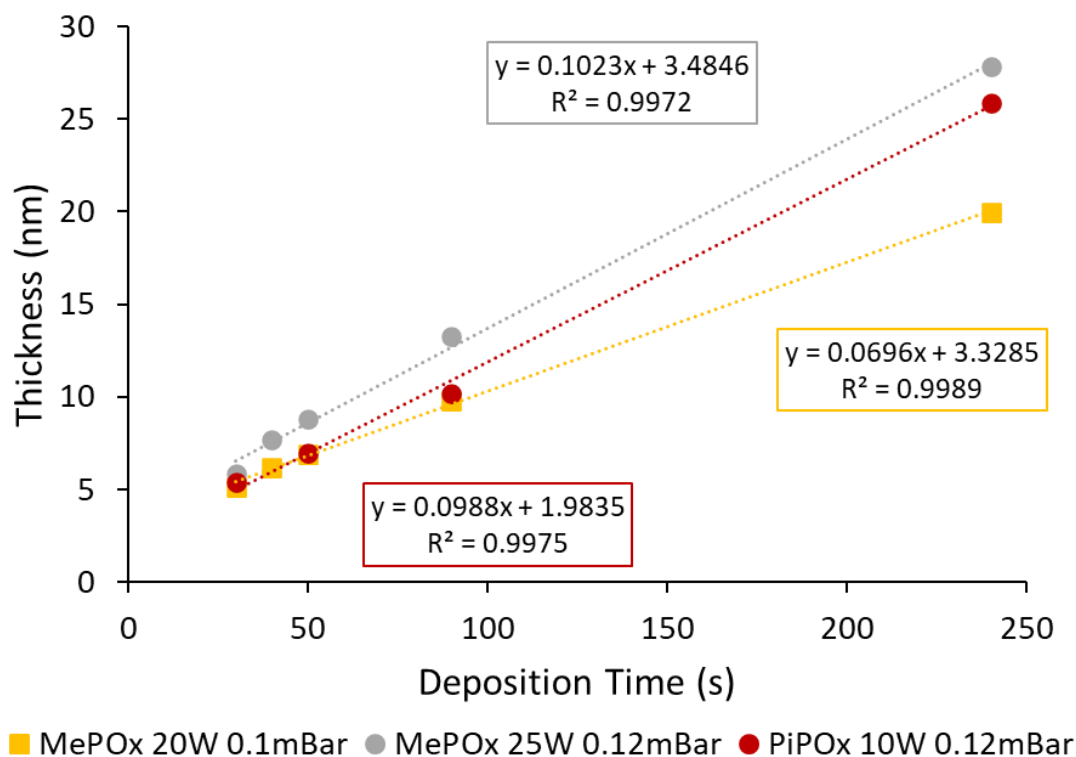


Figure S15: Relationship between deposition time and measured film thickness.

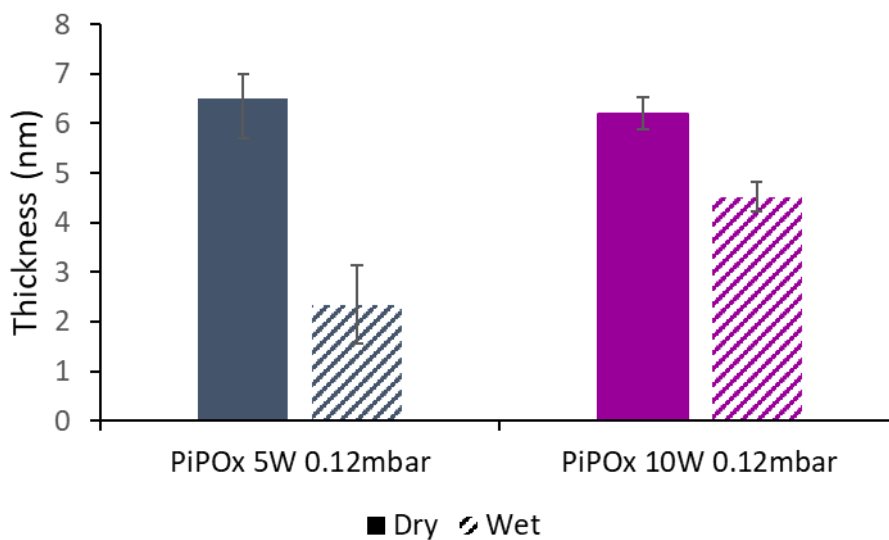


Figure S16: Thickness of PiPOx films before and after immersion in water for 1 hour. Stable films (such as PiPOx 10W 0.12mbar) lose approximately 1-2 nm of thickness after incubation, independent of initial thickness. Unstable films (PiPOx 5W 0.12mbar) lose a greater proportion of the initial thickness.

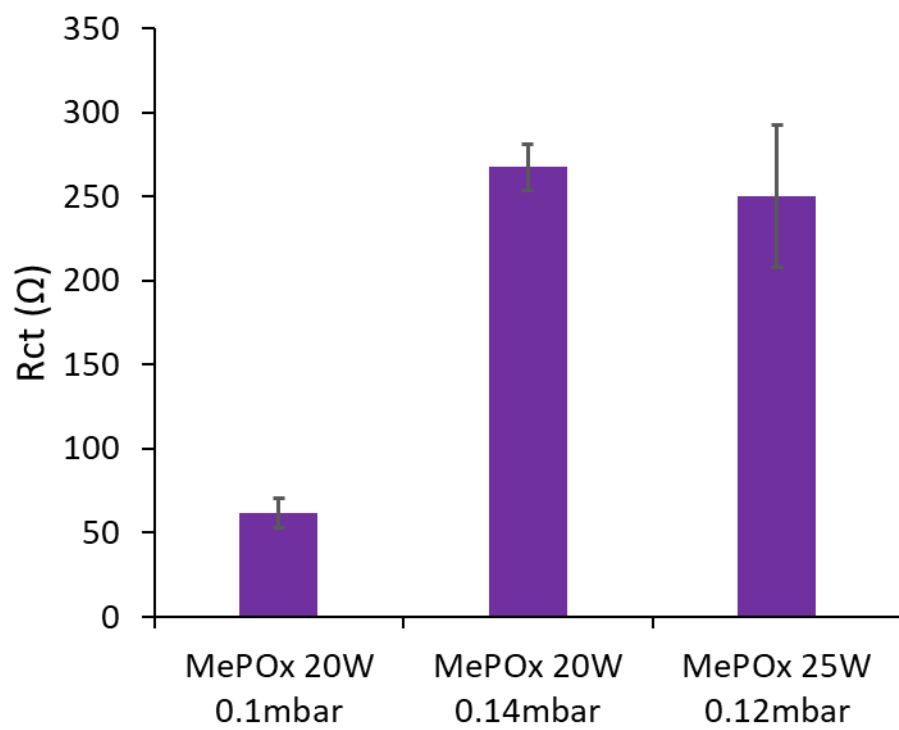


Figure S17: Influence of the top layer deposited onto PiPOx + 16 nm AuNP surfaces on the measured Rct.

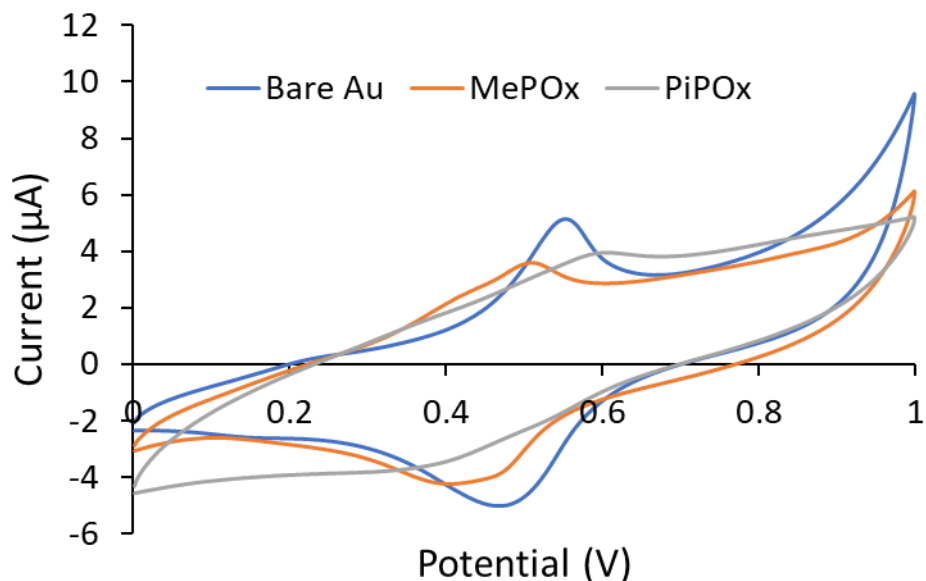


Figure S18: Representative cyclic voltammograms of surface bound electrochemical measurements.

Surprisingly, the presence of redox peaks in cyclic voltammetry (CV) measurements of these films (Figure S18) indicates that SAMs were able to be formed despite the conformal plasma polymer coating. There are multiple possible explanations for this, the first being the redox molecule was able to diffuse through the polymer during the 16 hour incubation used to form the SAM. Previous work has shown that plasma polymer films become more conductive over time during extended incubation periods, where the films could become more diffusive, allowing the electrolyte to penetrate further and reduce the R_{ct} . The second possibility is that, due to the complex chemistry of the plasma polymer films, the SAM may have been able to adsorb to the surface through the polymer rather than through an Au-S interaction. POx films have been demonstrated to have other reactive groups (than the oxazoline ring) on the surface that may contribute to ligand binding such as imine and nitrile groups.^{1,2} Lastly, the plasma polymer film could be discontinuous and there are pinholes that allow direct access to the gold. However, we have conducted extensive AFM studies to confirm that the films deposited here are continuous and pinhole free.³

References

- [1] M. N. Macgregor, A. Michelmore, H. Safizadeh Shirazi, J. Whittle, K. Vasilev *Chemistry of Materials*. **2017**, *29*, 8047-8051.
- [2] M. N. Macgregor-Ramiasa, A. A. Cavallaro, K. Vasilev *Journal of Materials Chemistry B*. **2015**, *3*, 6327-6337.
- [3] A. Gheorghiu, D. Yang, I. Delcheva, C. Priest, M. MacGregor *Plasma Processes and Polymers*. **2023**, *n/a*, e2200233.