

## Electronic Supplementary Information for:

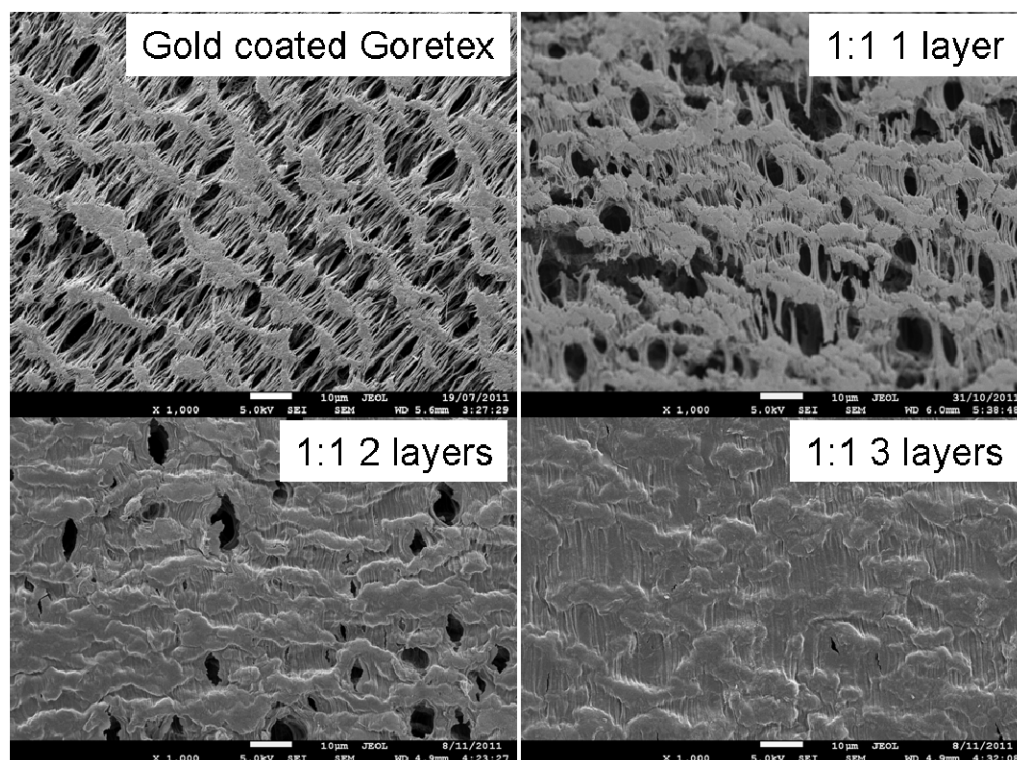
### Conducting Polymer Alloys for Photo-enhanced Electro-Catalytic Oxygen Reduction

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**Keywords:** Conducting Polymer Alloys, Photo-Electro-Catalysis, PEDOT, Polythiophene, Oxygen Reduction

#### *Gas diffusion electrode characterisation*

SEM images of different layer electrodes showed different coverage of the polymer alloys on the Goretex's surface (**Figure S1**). However, the coverage appeared to be the same for both (PEDOT:PTTh 1:1):PEG 0.5 and (PEDOT:PTTh 1:4):PEG 0.5. The sputter gold layer was very thin and not blocking the pores of the Goretex membrane. The 1 layer image showed very thin coverage whereas the 2 layers image showed the polymer alloys started to fill up the pore with thicker layer of the polymer alloys. The 3 layers image showed completed blocked pores without thickness (~ 240 nm) increased from the 2 layers electrode indicating the last layer was polymerized in between the pore but not on top of the existing layers.



**Figure S1** SEM images (top view) of (PEDOT:PTTh 1:1):PEG 0.5 and different number of layers.

This development in layer thickness/density, that is blocking the gas diffusion and thereby obstructing the desired 3 phase interface, is somewhat different from what has been seen for pure PEDOT films on similar Goretex® based electrodes and reflects the difference in the two-step deposition/polymerization procedure used in this work. Similarly, it cannot be assumed that the alloy formation is identical on substrates with so significantly different morphology as Au coated mylar and Au coated Goretex® explaining the apparent difference in optimal composition between dissolved oxygen measurements and the simple fuel-cell test.

It should be emphasized that the fuel-cell setup used in this work has not been optimized with regard to minimizing (electrolyte and electrode) resistance and the values should not be compared to traditional Pt/carbon/Nafion® cells. The setup only serves the purpose of verifying the effect of light on the oxygen reduction reaction on PEDOT:PTTh.

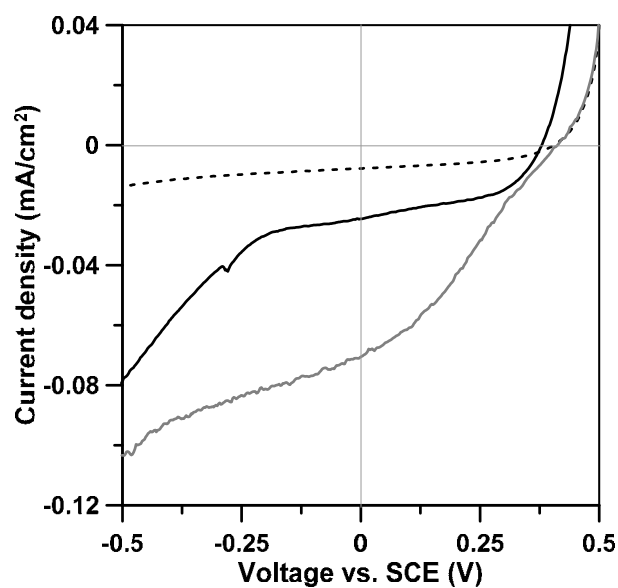
### ***Conductivity of PEDOT:PBTh:PEG and PEDOT:PTTh:PEG alloys***

**Table T1** shows the conductivity of various alloys. The decrease in conductivity with increase in PTTh or PBTh content is significantly larger than what would be explained by the simple dilution of the PEDOT component. This is attributed to a spontaneous charge transfer between PEDOT and PTTh or PBTh, where PEDOT is reduced further than under ambient conditions.

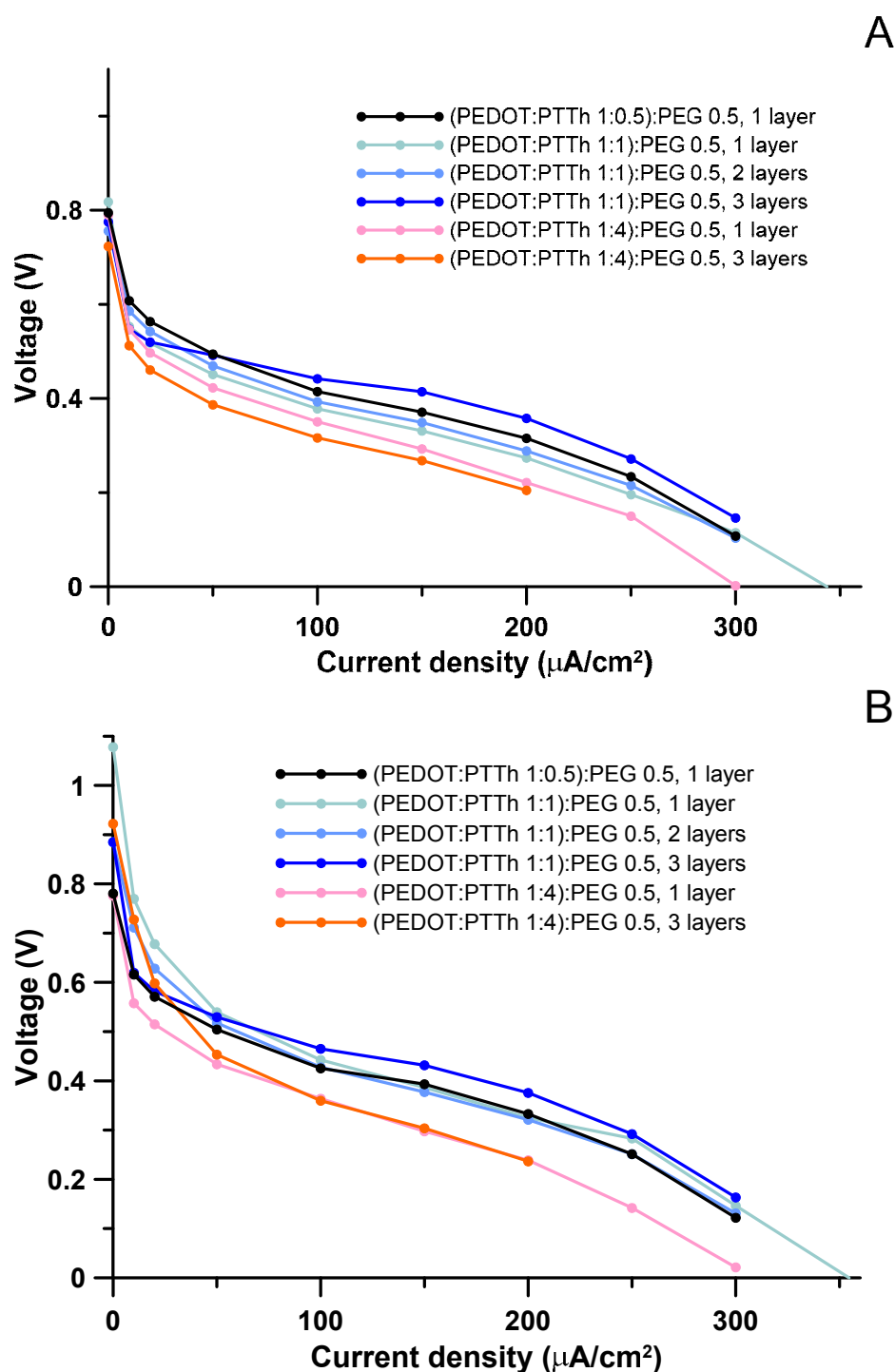
**Table T1** – Conductivity data of various ratios of PEDOT:PBTh:PEG and PEDOT:PTTh:PEG alloys

| <b>Material</b>            | <b>Conductivity [S/cm]</b> |
|----------------------------|----------------------------|
| PEDOT                      | 476                        |
| (PEDOT:PBTh 1:0.5):PEG 0.5 | 264                        |
| (PEDOT:PBTh 1:1):PEG 0.5   | 27                         |
| (PEDOT:PBTh 1:2):PEG 0.5   | 6                          |
| (PEDOT:PBTh 1:3):PEG 0.5   | 3                          |
| (PEDOT:PBTh 1:4):PEG 0.5   | 2                          |
| (PEDOT:PBTh 1:5):PEG 0.5   | 2                          |
| (PEDOT:PTTh 1:0.5):PEG 0.5 | 312                        |
| (PEDOT:PTTh 1:1):PEG 0.5   | 33                         |
| (PEDOT:PTTh 1:2):PEG 0.5   | 5                          |
| (PEDOT:PTTh 1:3):PEG 0.5   | 4                          |
| (PEDOT:PTTh 1:4):PEG 0.5   | 3                          |
| (PEDOT:PTTh 1:5):PEG 0.5   | 3                          |

***Light enhancement of oxygen reduction on PEDOT:PBTh in ratio 1:3***



**Figure S2** Current density-voltage curves at scan rate 1 mV/s of (PEDOT:PBTh 1:3):PEG 0.5, in 0.1 M Na<sub>2</sub>HPO<sub>4</sub> (adjusted to pH 10), dark and light (3470 W/m<sup>2</sup>); air bubbling into electrolyte dark - black line, air bubbling into electrolyte with light - grey line and N<sub>2</sub> bubbling into electrolyte dark - black dashed line.



**Figure S3** Comparison of different ratios of (PEDOT:PTTh 1:X):PEG 0.5 coated on gold/Goretex membrane and different number of layers in fuel cell setup in 0.1 M  $\text{Na}_2\text{HPO}_4$  (adjusted to pH 10). **A)** Tests were performed in dark and **B)** tests were performed under illumination (Leica KL 2500 LCD -  $3470 \text{ W}/\text{m}^2$ ).