# **Supporting Information**

2	Electrochemical hydrogen production on a metal-free polymer
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4	Roudabeh Valiollahi <sup>a</sup> , Mikhail Vagin <sup>a</sup> , Viktor Gueskine <sup>a</sup> , Amritpal Singh <sup>a,b</sup> , Sergey A. Grigoriev <sup>c</sup> ,
5	Artem S. Pushkarev <sup>c,d</sup> , Irina V. Pushkareva <sup>c,d</sup> , Mats Fahlman <sup>a,e</sup> , Xianjie Liu <sup>a</sup> , Ziyauddin Khan <sup>a</sup> ,
6	Magnus Berggren <sup>a,e</sup> , Igor Zozoulenko <sup>a,e</sup> , Xavier Crispin <sup>a,e*</sup>
7	<sup>a</sup> Laboratory of Organic Electronics, Department of Science and Technology, Linköping University,
8	SE-601 74 Norrköping, Sweden
9	<sup>b</sup> Department of Chemistry, Shoolini University, Solan, Himmachal Pradesh, India (Present address)
10	<sup>c</sup> National Research Centre "Kurchatov Institute", Kurchatov sq., 1, 123182, Moscow, Russia
11	<sup>d</sup> National Research University "Moscow Power Engineering Institute", Krasnokazarmennaya st., 14,
12	111250, Moscow, Russia
13	eWallenberg Wood Science Center, ITN, Linköping University, Norrköping, Sweden
14	*Corresponding author: <u>xavier.crispin@liu.se</u>
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17 Figure S1. XPS core level spectra of as-synthesized PEDOT-PEG films.



Figure S2. Experimental and fitted XPS S2p core level features of the as-synthesized PEDOT-PEG
film. The peak fitting used the standard procedure of asymmetric broadening of the spin-split doublet
to simulate the doping of the PEDOT-PEG film.

## **Supporting Note 1.**

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### In-situ conductivity calculations

For the *in-situ* conductivity measurements of the electroactive polymer, we employed a setup 28 29 originating from the works of Wrighton's group <sup>1,2</sup>. The polymer is electrodeposited, while for our work via vapor phase polymerization (VPP), onto two interdigitated working electrodes (WE I and 30 WE II) that can be polarized independently by a bipotentiostat. During linear potential sweep, a small 31 bias between WE I and WE II,  $\Delta E = E II - E I$  (typically  $\Delta E = +50 \text{ mV}$  in this work) is maintained. The 32 resistance, the inverse of conductivity, of the polymer film between the electrodes, R<sub>p</sub>, is evaluated as 33  $R_p = \Delta E/i_p$  where  $i_p$  is the channel current between WE I and WE II. However, this channel current is 34 not directly measurable, so its evaluation requires some sort of model. In spite of wide applicability of 35 this approach, there is surprisingly little discussion of the adopted approximations. A notable exception 36 is the work from the Uppsala group<sup>3</sup>, in which an explicit analysis is presented. Our analysis is largely 37 based on this work, but our conclusions are somewhat different. The specific resistance can be 38 39 determined by normalizing to the film thickness.

In the context of this study, two very different regimes of *in-situ* conductivity measurement are sweeped: (i) in the anodic region, there is virtually no electrochemical reaction, the doped PEDOT is conducting, so the currents measured by the potentiostat are dominated by the channel current rather than by faradaic currents; (ii) in the cathodic region, PEDOT is progressively dedoped, so its conductivity and channel current presumably decrease, but at the same time faradaic currents due to HER increase. In this situation, we need clear understanding what we maintain and what we neglect in our models.

47 The circuit analysis from Ref.<sup>3</sup> yields for the channel current:

48 
$$2 i_p = (i^{II} - i^{I}) - (i_F^{II} - i_F^{I})$$
 (1)

49 where  $i^{I}$  and  $i^{II}$  are the currents at WE I and WE II measured by the bipotentiostat, while  $i_{F}^{I}$  and  $i_{F}^{II}$  are 50 faradaic currents at these electrodes, unmeasurable in the presence of the channel current. The working 51 formula used in that work to calculate the channel current is:

52 
$$i_p = (i^{II} - i^{I})/2$$
 (2)

53 which implies the quality of faradaic currents through both working electrodes,  $i_F^{II} = i_F^{I}$ , throughout 54 the biased scan,  $\Delta E \neq 0$ .

55 While this approximation might work in certain cases, we cannot take it for granted because, (i) the 56 polymer film portions responding through WE I and WE II can be different from each other and (ii) 57 be it not the case,  $\Delta E$  can cause some difference in faradaic current of the same polymer electrode, as 58 reflected in its polarization curve.

59 We note first that during "zero-bias scan", that is, both working electrodes at the same potential at any 60 time,  $\Delta E=0$ , which will be denoted by subscript "0", the channel current vanishes,  $i_{p0} = 0$ , which 61 implies that the faradaic currents at both electrodes are measured:

$$62 \quad i_0^{\ I} = i_{F0}^{\ I}, \ i_0^{\ II} = i_{F0}^{\ II}. \tag{3}$$

63 Next, we take it for granted that faradaic current at WE I depends only on its own potential and not on64 the potential of the other electrode, WE II; that is:

65 
$$i_F^{\rm I} = i_{F0}^{\rm I} = i_0^{\rm I}$$
, (4)

66 taking for WE I the same potentials during the biased and zero-bias scans and using also (3).

67 Now the only remaining unknown and unmeasurable term in (1) is  $i_F^{II}$ . In order to express it, note that: 68

69 
$$i^{II} + i^{I} = i_{F}{}^{II} + i_{F}{}^{I}$$
 (5)

70 as both sums represent the total current through the counter electrode. Then:

71 
$$i_F^{II} = i^{II} + i^I - i_F^{II} = i^{II} + i^I - i_0^{II}$$
 (6)

72 where identity (4) was also used. Substituting (6) into (1) we obtain:

73 
$$i_p = i_0^{\rm I} - i^{\rm I}$$
 (7)







Figure S3. Doping of semiconductor catalyst by HER. The voltammetry (A) and in-situ resistometry (B) on PEDOT-PEG-film in acidic electrolyte ( $0.5 \text{ M H}_2\text{SO}_4$ , 5 mV s<sup>-1</sup>, biased (50 mV, red curve) and zero-biased (black curve) film-modified gold interdigitated electrode).



Figure S4. pH effect of PEDOT-PEG *in-situ* conductivity. (A) Cyclic voltammogram of PEDOT in 1.0 M KCl (scan rate 5 mV s<sup>-1</sup>). (B) *In-situ* resistometry were performed on PEDOT-PEG-modified interdigitated electrodes in nitrogen-saturated 1.0 M KCl or 0.5 M H<sub>2</sub>SO<sub>4</sub> (black or red curves, respectively; scan rate 5 mV s<sup>-1</sup>).

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![](_page_7_Figure_0.jpeg)

Figure S5. HER electrocatalysis on PEDOT-PEG. IR-compensated steady-state polarization curves
obtained on bare and PEDOT-PEG-modified GCE (black and red symbols, respectively; rotating disk
electrode, 900 rpm; 0.5 M H<sub>2</sub>SO<sub>4</sub>; oxidation and reduction currents as open and filled symbols,
respectively).

![](_page_8_Figure_0.jpeg)

97 Figure S6. HER electrocatalysis on PEDOT-PEG. IR-compensated steady-state polarization curve
98 obtained on PEDOT-PEG-modified GCE (rotating disk electrode, 900 rpm; 0.5 M H<sub>2</sub>SO<sub>4</sub>).

![](_page_9_Figure_0.jpeg)

![](_page_9_Figure_1.jpeg)

102 Figure S7. Free energy profiles for the HER on PEDOT for the Volmer-Tafel mechanism (Red) and the Volmer-Heyrovsky mechanism (Green)

103 as obtained from Gaussian calculations with gas phase thermochemical corrections.

# **Supporting Note 2.**

### 107 Quantum chemical calculations

![](_page_10_Figure_2.jpeg)

108 Scheme S1. Reactions steps of heterogeneous HER

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Our starting point is DFT calculations (Gaussian 09 Revision E.01 wB97XD functional and 6-31G(d) 110 basis set)<sup>4</sup> leading to the optimized structures, transition states, and their electronic energies. While 111 studying the hydrogenated PEDOT intermediates, we considered the possibility of hydrogen addition 112 to  $\alpha$ - (next to sulfur) and  $\beta$ - carbon atoms of the thiophene ring. It turned out that  $\alpha$ -addition was 113 slightly favored. However, this  $\alpha$ -hydrogenated intermediate was strongly geometrically distorted in 114 comparison to the initial oligomer chain. This distorted geometry was obtained by single-molecule 115 optimization in a gas phase, but one should not lose from view that the real object of our modeling is 116 117 the oligomer inside a thin film in a solid phase, where this distortion would not be possible because of 118 the presence of neighboring oligomers (for details of the morphology of PEDOT thin films see *e.g.* Refs <sup>5-7</sup>). Given the small energy preference, and the fact that the distortion would not be feasible in 119 the solid state, we concentrated exclusively on  $\beta$ - hydrogenated intermediates preserving the initial 120 PEDOT chain conformation. 121

At the next stage, the gas phase free energies at 25 °C are obtained with thermochemical corrections as implemented in Gaussian (Fig. S7). Note that free electrons in this case are exchanged with infinity (which is electrodes in our case), and their energy is 0 eV. In this way, the gas-phase free energy diagrams for both reaction pathways are obtained.

126 In order to arrive from the Gaussian free energies at electrochemically relevant free energies, we rely127 on the thermodynamic data listed below.

128 Reference data

- 129 1. Hydrogen atom ionization: 13.60 eV<sup>8</sup>
- 130 H(g)  $\rightarrow$  H<sup>+</sup><sub>(g)</sub> + e<sub>(inf)</sub>
- 131 2. Hydrogen molecule dissociation: 4.48 eV
- 132 36 118.0 cm-1 =  $36118.0/8065.5 \text{ eV} = 4.48 \text{ eV}^9$
- 133  $H_{2(g)} \rightarrow H_{(g)} + H_{(g)}$
- 134 3. Proton hydration:  $-11.39 \text{ eV}^{10}$

- 135  $\Delta G_{hvd298}(H^+) = -262.4 \text{ kcal/mol} = -11.39 \text{ eV}$
- 136  $H^+_{(g)} \rightarrow H^+_{(s)}$
- 137 4. Proton affinity of  $H_2O$ : -7.18 eV <sup>11</sup>

138  $H_2O_{(g)} + H^+_{(g)} \rightarrow H_3O^+_{(g)}$ 

- 139 5. Water molar free energy of vaporization: 0.10 eV
- 140  $H_2O_{(l)} \rightarrow H_2O_{(g)}$
- 141 Water molar enthalpy of vaporization:
- 142 45.051 kJ mol<sup>-1</sup> (0 °C), 40.657 kJ mol<sup>-1</sup> (100 °C)
- 143 extrapolated to 43.952 kJ mol<sup>-1</sup> = 0.46 eV (25 °C) <sup>12</sup>:
- 144 As at 100 °C,  $\Delta G_{vap} = \Delta H_{vap} T\Delta S_{vap} = 0$ ,
- 145  $\Delta S_{vap} = \Delta Hvap / T = 0.4555 \text{ eV} / 373 \text{ K} = 1.22 * 10^{-3} \text{ eV/K}$ , weakly dependent on T.

146 At 25 °C, 
$$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap} = 0.46 \text{ eV} - 298 * 1.22 * 10^{-3} = 0.10 \text{ eV}$$

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First of all, in order to check the compatibility of the thermodynamic data from the literature with our gas-phase thermodynamic values from Gaussian, we calculate the free energy of the overall reaction from the former, using the method of thermodynamic cycles, as the total change of a thermodynamic potential does not depend on path leading from the reactants to the products.

- 152 Therefore, the reaction  $2H_3O^+_{(g)} + 2e_{(inf)} \rightarrow 2H_2O_{(g)} + H_{2(g)}$  can be replaced by the following sequence,
- 153 with the free energies from the Reference data above:

154	$2H_{3}O^{+}_{(g)} \rightarrow 2H_{2}O_{(g)} + 2H^{+}_{(g)}$	$\Delta G = 2 * 7.18 = +14.36 \text{ eV}$
155	$2\mathrm{H^{+}}_{(\mathrm{g})} + 2\mathrm{e}_{(\mathrm{inf})} \rightarrow 2\mathrm{H}_{(\mathrm{g})}$	$\Delta G = 2 * (-13.60) = -27.20 \text{ eV}$
156	$2H_{(g)} \rightarrow H_{2(g)}$	$\Delta G = -4.48 \text{ eV}$
157	$\overline{2H_3O^+_{(g)} + 2e_{(inf)} \rightarrow 2H_2O_{(g)} + H_{2(g)}}$	$\Delta G = -17.32 \text{ eV}$

158 where (g) stands for the gas phase, and the energy of electrons at infinity,  $e_{(inf)}$ , is zero. This value is 159 to be compared to the free energy change from reactants to the final products from the Gaussian 160 calculations, which is -17.12 eV. Note that PEDOT does not intervene in the free energy calculations 161 because it returns to initial state at the end of the cycle, as a catalyst should do. Our gas phase free 162 energy change is therefore in excellent agreement with independent thermodynamic data. However, 163 electrochemical conditions in aqueous solution are very different energetically.

164 Two independent transformations of the free energies obtained from Gaussian calculations towards165 electrochemically relevant free energies are necessary, namely:

166 i) From electrons at infinity to electrons at a chosen electrochemical (redox) potential vs. a reference

167 electrode, ii) From gas phase to aqueous solution.

168 To this end, we use the approach of thermodynamic cycles, as the free energy change is independent 169 of the path between the reactants and the products.

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#### 171 Absolute potential of SHE

For the first transformation, we need to refer the energy of the electrons at a given redox potential to the absolute scale, with zero energy at infinity. In practice, we obtain the energy of electrons corresponding to 0 V vs. SHE, in other words, the absolute potential of SHE. We start by calculating the free energy of molecular hydrogen oxidation in aqueous solution at 25 °C involving, however, the electrons going to infinity when they leave the molecule. The reaction is:

177  $H_{2(g)} \rightarrow 2H^+_{(s)} + 2e_{(inf)}$ 

178 And it can be replaced by the following sequence, for which the free energies are taken from the

179 reference data above

180	$H_{2(g)} \rightarrow 2H_{(g)}$	4.48 eV
181	$2H_{(g)} \rightarrow 2H^+_{(g)} + 2e_{(inf)}$	2 * 13.60 eV
182	$2\mathrm{H^{+}_{(g)}} \rightarrow 2\mathrm{H^{+}_{(s)}}$	-2 * 11.39 eV
183	$\overline{H_{2(g)} \rightarrow 2H^{+}_{(s)} + 2e_{(inf)}}$	8.90 eV

184 This reaction has a positive  $\Delta G$ , with the products lying higher at the free energy scale than the

products. At equilibrium,  $\Delta G = 0$ , which is the case of SHE. Therefore, to attain equilibrium in molecular hydrogen oxidation, we need to lower the energy of the products by 8.90 eV. This is attained by placing two liberated electrons not at infinity with E = 0, but at the free energy level (Fermi level) of -8.90 / 2 = -4.45 eV. This Fermi level corresponds therefore to the electrochemical potential of 0 V vs. SHE:

- 190 SHE (pH0, 25 °C)  $H_{2(g)} \leftrightarrow 2H^+_{(s)} + 2e_{(SHE)}$ :  $\Delta G = 0$  (equilibrium)
- 191 Note that the IUPAC reference value is -4.44 eV<sup>12</sup> confirming the exactness of our thermodynamic
- 192 approach. This means that in order to construct free energy diagrams at 0 V vs. SHE, -4.45 eV per free
- 193 electron should be added when calculating the free energy balance. Solvation free energy of  $H_3O^+$ :
- 194  $H_3O^+_{(g)} \rightarrow H_3O^+_{(s)}$  can be replaced by the sequence:
- 195  $H_3O^+_{(g)} \rightarrow H_2O_{(g)} + H^+_{(g)}$  +7.18 eV
- 196 H<sub>2</sub>O<sub>(l)</sub> → H<sub>2</sub>O<sub>(g)</sub> -0.10 eV
- 197  $H^+_{(g)} \rightarrow H^+_{(s)}$  -11.39 eV
- 198  $\overline{\mathrm{H}_{3}\mathrm{O}^{+}_{(\mathrm{g})}} \rightarrow \mathrm{H}_{3}\mathrm{O}^{+}_{(\mathrm{s})}$  -4.31 eV

For PEDOT and intermediates involving PEDOT, we do not use any solvation energies considering that in reality these are not single molecules surrounded by the solvent but the surface of the bulk. Reliable thermodynamic estimation of the changes in free energies due to partial solvation of such surface moieties is not feasible, and we prefer to refrain from arbitrary corrections here.

In summary, in order to obtain an electrochemically relevant free energy diagram from the Gaussianfree energies, we need to add the following stabilization (negative) energy terms:

- 205 for each free electron:  $\Delta \text{Ee} = -4.45 \text{ eV}$
- 206 for each  $H_3O^+$ :  $\Delta EH_3O^+ = -4.31 \text{ eV}$
- 207 for each H<sub>2</sub>O:  $\Delta EH_2O = -0.10 \text{ eV}$
- 208

209 In this way, the free energy diagram in the main text is obtained, for the numerical values for both the

210 gas phase and the electrochemical free energy diagrams see Table S1 below. For an illustration 211 consider, for example, Step 1 in VT and VH mechanisms:

212 PEDOT<sup>0</sup> + 2H<sub>3</sub>O<sup>+</sup> + 2e  $\rightarrow$  PEDOT<sup>0</sup>-H + H<sub>2</sub>O + H<sub>3</sub>O<sup>+</sup> + e

The free DFT energy calculation in the gas phase for this step gives EDFT= -7.83 eV. At this step one free electron and one solvated hydronium are consumed, and one water molecule is added to solution. This leads to the correction  $\Delta E = -\Delta E e - \Delta E H_3 O^+ + \Delta E H_2 O = +4.45 + 4.31 - 0.10 = 8.66 eV$ , which results in the free energy E = -7.83 + 8.66 = 0.83 (eV) for the aqueous phase and free electrons from SHE.

- 218 Table S1. Free energies (eV, relative to the reactants) for Volmer-Heyrovsky (VH) and Volmer-
- 219 Tafel (VT) mechanisms.

	VH	VH		VT	VT
	gas inf	aq SHE		gas inf	aq SHE
$PEDOT^0 + 2H_3O^+ + 2e$	0.0	0.0	$PEDOT^0 + 2H_3O^+ + 2e$	0.0	0.0
$PEDOT^{0}-H+H_{2}O+H_{3}O^{+}+e$	-7.83	0.83	$PEDOT^{0}-H+H_{2}O+H_{3}O^{+}$	-7.83	0.83
			+ e		
			$H-PEDOT^0-H + 2H_2O$	-15.97	1.35
$PEDOTHH_{3}O^{+} + H_{2}O + e$	-6.31	2.35	$H PEDOT^0 H + 2H_2O$	-12.42	4.90
(TS+)			(TS)		
$PEDOTHH_3O^0 + H_2O + e$	-13.15	0.04			
(TS0)					
$PEDOT^0 + H_2 + 2H_2O$	-17.14	0.18	$PEDOT^0 + H_2 + 2H_2O$	-17.12	0.20

![](_page_15_Figure_6.jpeg)

221 aqueous phase, free electrons at the Standard Hydrogen Electrode free energy.

![](_page_16_Figure_0.jpeg)

Figure S8. Schematic diagram of the PEMWE. 1 – cell holders with flow-field plates; 2 – fittings for
reactant/products supply/removal; 3 – fittings for heating/cooling; 4 – Nafion<sup>®</sup> membrane; 5 – current
collectors/gas diffusion electrodes (porous titanium discs); 6 – sealants; 7 – electrocatalytic layers.

![](_page_17_Figure_0.jpeg)

237 Figure S9. Cyclic voltammograms obtained for PEDOT-PEG electrode in nitrogen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>

238 with a glassy carbon counter electrode. Scan rate 5 mV s<sup>-1</sup>.

![](_page_18_Figure_0.jpeg)

Figure S10. Cyclic voltammograms of a GCE in a ferrocene containing 0.1 M TEAP in anhydrous ACN
solution used to calibrate the Pt-quasi reference electrode (scan rate 5 mV s<sup>-1</sup>). The measurement was performed
in a glovebox under inert conditions.

### 245 References

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- Kittlesen, G. P., White, H. S. & Wrighton, M. S. Chemical derivatization of microelectrode arrays by
   oxidation of pyrrole and N-methylpyrrole: fabrication of molecule-based electronic devices. *Journal of the American Chemical Society* **106**, 7389-7396, doi:10.1021/ja00336a016 (1984).
- 250 2 Chao, S. & Wrighton, M. S. Solid-state microelectrochemistry: electrical characteristics of a solid 251 state microelectrochemical transistor based on poly(3-methylthiophene). *Journal of the American* 252 *Chemical Society* 109, 2197-2199, doi:10.1021/ja00241a057 (1987).
- Karlsson, C., Huang, H., Strømme, M., Gogoll, A. & Sjödin, M. Ion- and Electron Transport in
   Pyrrole/Quinone Conducting Redox Polymers Investigated by In Situ Conductivity Methods.
   *Electrochimica Acta* 179, 336-342, doi:<u>https://doi.org/10.1016/j.electacta.2015.02.193</u> (2015).
- 256 4 Frisch, M. J. *et al.* (Wallingford CT, 2009).
- Franco-Gonzalez, J. F. & Zozoulenko, I. V. Molecular Dynamics Study of Morphology of Doped
  PEDOT: From Solution to Dry Phase. *The Journal of Physical Chemistry B* 121, 4299-4307,
  doi:10.1021/acs.jpcb.7b01510 (2017).
- Modarresi, M., Franco-Gonzalez, J. F. & Zozoulenko, I. Morphology and ion diffusion in
  PEDOT:Tos. A coarse grained molecular dynamics simulation. *Phys Chem Chem Phys* 20, 1718817198, doi:10.1039/c8cp02902d (2018).
- Franco-Gonzalez, J. F., Rolland, N. & Zozoulenko, I. V. Substrate-Dependent Morphology and Its
  Effect on Electrical Mobility of Doped Poly(3,4-ethylenedioxythiophene) (PEDOT) Thin Films. ACS *Appl Mater Interfaces* 10, 29115-29126, doi:10.1021/acsami.8b08774 (2018).
- 266 8 <<u>https://webbook.nist.gov/cgi/cbook.cgi?ID=C12385136&Mask=20</u>>(
- Zhang, Y. P., Cheng, C. H., Kim, J. T., Stanojevic, J. & Eyler, E. E. Dissociation Energies of
  Molecular Hydrogen and the Hydrogen Molecular Ion. *Physical Review Letters* 92, 203003,
  doi:10.1103/PhysRevLett.92.203003 (2004).
- Zhan, C.-G. & Dixon, D. A. Absolute Hydration Free Energy of the Proton from First-Principles
   Electronic Structure Calculations. *The Journal of Physical Chemistry A* 105, 11534-11540,
   doi:10.1021/jp012536s (2001).
- 273 11 Ng, C. Y. et al. Photoionization of dimeric polyatomic molecules: Proton affinities of H<sub>2</sub>O and HF.
- 274 The Journal of Chemical Physics 67, 4235-4237, doi:10.1063/1.435404 (1977).
- 275 12 <<u>https://webbook.nist.gov/cgi/cbook.cgi?ID=C12385136&Mask=20</u>>