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Valiollahi Bisheh, R., Vagin, M., Gueskine, V., Singh, A., Grigoriev, S. A., Pushkarev, A. S., Pushkareva, I. V., Fahlman, M., Liu, X., Khan, Z., Berggren, M., Zozoulenko, I., Crispin, X., (2019), Electrochemical hydrogen production on a metal-free polymer, *SUSTAINABLE ENERGY and FUELS*, 3(12), 3387-3398. <https://doi.org/10.1039/c9se00687g>

Original publication available at:

<https://doi.org/10.1039/c9se00687g>

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Electrochemical hydrogen production on a metal-free polymer

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Abstract

The exploration for true electrocatalytic reactions at organic conducting polymer electrodes, including chemisorption of a reactant and desorption of a product, undergoes a renewed interest due to the profound implication it could have on low-cost large area electrochemical energy technology. Here, we finalize the debate about the ability that an organic electrode, more specifically poly(3,4-ethylenedioxythiophene (PEDOT), to be an electrocatalyst for the hydrogen production. This paper proves and covers fundamental studies of the hydrogen evolution reaction (HER) on PEDOT films. Both, theory based on DFT (Density Functional Theory) and experimental studies using electrochemical techniques and *in-operando* mass spectroscopy suggest a Volmer-Heyrovsky mechanism for the actual HER on PEDOT. It is shown that PEDOT reaches a comparable exchange current density as metals (*i.e.* Cu, Ni, Au) and in addition does not form passivating oxide layers and

suffer from chemical corrosion in acidic media. Finally, an electrolyzer stack using the organic polymer electrode demonstrates the HER-performance in real applications.

Introduction

The importance of H₂ as an energy carrier in the future society is not only restricted to serving us as a high energy density fuel for transportation, but is also an enabler for large scale energy storage in order to *e.g.* damp the mismatch between availability of electrical energy, generated from power plants (sun or wind), and societal demands for electricity. Today, H₂ is produced by steam-methane reforming ¹: $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$. The extraction of the fossil gas is expected to face a peak, giving that in the future H₂ will most likely be produced, in a cost-competitive manner, via water electrolysis. Water electrolysis is the electrochemical decomposition of water into oxygen and hydrogen gas driven by an electric current: $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$. A vision for green future H₂ power plants is that the electricity, required to drive the actual water electrolysis, should come from solar, wind or other renewable sources converted into electricity. An advantage of water electrolysis is the purity of the resulting H₂ gas. H₂ obtained from methane reforming needs to be purified to remove carbon monoxide which poisons the Pt catalyst in the fuel cells ².

H₂ production from water is realized in devices termed *electrolyzer*. There are two main electrolyzer technologies available on the market, the alkaline and the proton exchange membrane (PEM) electrolyzers, respectively. An electrolyzer is based on two catalytic metal electrodes and an electrolytic membrane. Water electrolysis is then simply obtained by applying a voltage (1.23 V + overvoltage) between the two electrodes. The electrodes are composed of catalysts to minimize the overvoltage, which represent one of the major losses in energy efficiency. In an acidic medium, the cathode catalyzes the half-reaction $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$ and the anode catalyzes the oxidation $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$. Today, commercial electrolyzer efficiencies typically reaches the range of about 62–82% and 67–82% for the alkaline and PEM types, respectively ³. One of the key

features that limits a widespread use of electrolyzers as a main technology for H₂ production is the need for noble metal catalysts (*e.g.* platinum) in the electrolyzer electrodes. Noble metals are utterly expensive, because of their low natural abundance. Hence, the search for platinum group metal (PGM)-free heterogeneous catalysts ⁴⁻¹³ for H₂-producing electrolyzers is thus highly desired.

The hydrogen evolution reaction (HER) performed via aqueous proton reduction is considered a gold-standard in general electrocatalysis, as originated by the centennial work by J. Tafel ¹⁴. On a Pt electrocatalyst, HER occurs in a two-step mechanism ¹⁵. The fast first step is a proton electrosorption discharge leading to an adsorbed H atom (Volmer reaction): $H^+ + e^- \rightarrow H_{ads}$. The rate determining step is the following recombination of two adsorbed atoms (Tafel reaction): $H_{ads} + H_{ads} \rightarrow H_2$, or an electrochemical desorption step (Heyrovsky reaction): $H_{ads} + H^+ + e^- \rightarrow H_2$. A true electrocatalytic reaction implies chemisorption of the reactant and desorption of the product. The rate of HER of various metals has often been related to the energetics of the chemisorption of H_{ads}. The exchange current density of the HER span from 10⁻⁹-10⁻⁸ A/cm² for Pb, Zn, Sn to 10⁻⁴-10⁻³ A/cm² for Pt, Ir, Rh ¹⁶.

In the search for new earth abundant electrocatalyst materials, one mysterious finding was done in 2010 by Winther-Jensen et al. who proposed that organic conducting polymers, such as poly(3,4-ethylenedioxythiophene) PEDOT, can serve as an electrocatalyst for the HER ¹⁷. They reported that a PEDOT layer does not promote HER. However, when PEDOT is blended with a copolymer PEG (Poly(ethylene glycol)), the resulting conducting polymer film “PEDOT-PEG” deposited on a Ti electrode displays a clear signal of H₂ evolution that surprisingly also enhances with time. This discovery was attributed to the ability of PEG to coordinate protons and thereby to bring them into close proximity to the PEDOT, thus allowing the reduction to occur and hydrogen to be produced. But soon after, Bard et al. made a study of the same polymer layer PEDOT-PEG on Au and Ti and suggested that the polymer film was porous and that its porosity increased with time when the electrode was immersed in solution, while the hydrogen evolution catalysis then takes place on the conducting

substrate beneath the polymer rather than on or within the PEDOT-PEG film¹⁸. Despite this intriguing debate, scientists went further on and used PEDOT as a mixed ionic-electronic conducting matrix to embed inorganic catalytic nanoparticles (*e.g.* Pt-Pd^{19,20}, WS₂²¹, V₂Se₉²²) to boost the HER. Hence, today it is still not clear if a conducting polymer such as PEDOT-PEG can be seen as electrocatalyst for HER or not. But recent studies pointed out that PEDOT-PEG has a semi-metallic nature^{23,24}. In order to truly state electrocatalysis, a conducting polymer must then adsorb a reactant on its surface and desorb a product, in the manner as it has been demonstrated recently for the oxygen reduction reaction on PEDOT²⁵. Those last findings re-dynamize the debate about using conducting polymers as a potential electrocatalyst for HER.

In this report, we demonstrate that the PEDOT-PEG composite, coated on inert glass substrates, is conducting enough to truly generate H₂, via HER, in the cathodic regime without the need for any underlying metallic conducting layer. This truly demonstrates that conducting polymers are directly involved in the HER. Moreover, the onset potential of the HER is only 4 mV larger than the overpotential using a Pt electrode and the exchange current density reaches 10 $\mu\text{A}/\text{cm}^2$, *i.e.* a larger current density achieved with transition metals (Cu, Ni, Co), which thus demonstrates that a true electrocatalytic process is governing the HER. The electrocatalytic reaction was modelled with density functional theory (DFT) calculations indicating a possible two step Volmer-Heyrovsky reaction pathway. Finally, we report the first electrolyzer including a polymer electrode to produce H₂ with a rate reaching the same order of magnitude when comparing with a Pt electrode.

Results and discussion

In order to investigate the HER on polymer electrodes made from the PEDOT-PEG polymer blend, we first synthesized PEDOT⁺OTf⁻ via vapor phase polymerization, according to a recently published recipe²⁶, on glass substrates. PEDOT is a conjugated polymer turned oxidized during

synthesis such that its π -electron system carries positive charges that are balanced by the trifluoromethanesulfonate (OTf) counterions. The electrode film was prepared by exposing a vapor of the EDOT monomer to a film made of a blend of the oxidant $\text{Fe}(\text{OTf})_3$ and the triblock copolymer PEG-PPG-PEG (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)). The copolymer makes the film waxy and acts as a template for polymerization and film growth, thus promoting good packing of PEDOT chains ²⁷ by providing a "Structure-directed" growth, which also leads to achieve a higher electrical conductivity²⁸. The polymerization is spontaneous and results in a functional electrode film that we here term "PEDOT-PEG". Finally, the electrode sample is cleaned in a solution of HCl to remove iron salt from the electrode surface and bulk. The film thickness was estimated by atomic force microscopy (AFM) and reached about 43 nm with a corresponding root mean square roughness of 16 nm (Fig. 1B) and its electrical conductivity was estimated using a four-point probe setup and hits a value of about 1200 S/cm. At the molecular level, the charge carrier transport is promoted by the formation of local crystalline nanodomains, expressing metallic conductivity, composed of stacks of tenths of PEDOT chains bounded by interchain π - π interactions ²⁹. The charge transport is then governed by thermally activated hopping between the crystalline nanodomains ^{30,31}. On a macroscopic level, AFM images reveal a porous network of interconnected polymer filaments which provides a continuous pathway to conduct holes (Fig. 1B). Hence, the polymer film has an attractive morphology that provides a very large solid-electrolyte interface spontaneously structured in the nanoscale. Surface analysis of the polymer films, when exposed to air, was conducted using XPS (Fig. S1) and reveals absence of any oxide surface layer along the outermost surface structures of the polymer electrode. This is a significant difference with non-noble metals or inorganic semiconductors and this ensures a clean interface between the PEDOT-PEG electrode and the aqueous solution and its components. The absence of fluoride-associated XPS signals, originating from the initial counter-ion (trifluoromethanesulfonate, OTf), suggests an effective ion exchange during the washing step that then yields chloride-doped polymer films. The ratio between the thiophene

sulfur content quantified from the S2p peak (Fig. S2) and the content of chloride counter-ion (Cl 2p) gives an estimation of the polymer doping level of *ca.* 20%.

The conducting polymer film electrode, manufactured on glass, was placed in an aqueous electrolyte and was then polarized by a potential applied with respect to a reference electrode. A significant capacitive current was recorded when performing voltammetry measurements within the potential window of [+0.3 V to +0.9 V] (Fig. S4A). This region of applied potential is featured with a potential-independent (*i.e.* non-faradaic) current, which produces box-shaped voltammograms reminiscent of the mixed ionic-electronic conducting characteristics of the polymer electrodes, typically found in polymer supercapacitors ²⁶. The capacitive current $I_C = C dV/dt$ is related to the charge-balancing process residing between the polymer electrode (carrying electronic charges) and the electrolyte (transporting ions) on the applied potential ramp (dV/dt).

The electrical conductivity of PEDOT-based films, provided throughout a wide range of oxidation levels, enables the direct exploration of its electrocatalytic properties without the need of an additional conducting substrate. Importantly for HER, the application of a negative bias voltage on the conducting polymer electrode, in an electrolyte environment, causes simultaneously both interior and heterogeneous electron transfer.

Firstly, the electroreduction process on the PEDOT⁺Cl⁻ chains, upon negative polarization, leads to a progressive transition from a positively doped and highly conductive state to a dedoped close to insulating state (PEDOT⁺Cl⁻ + e⁻ → PEDOT⁰ + Cl⁻). This is also evident from electrochromism experiments as the PEDOT film changes its color from bright blue to dark blue ³². This doped-to-dedoped semiconductor transition was characterized by resistometry and resulted in a rise in resistance of the PEDOT film (Fig. 2A). The normalized PEDOT film resistance was measured in acidic (0.5 M H₂SO₄), neutral (1.0 M KCl) and aprotic (0.1 M TEAP in I) solutions, with Pt and Ag/AgCl as counter and reference electrode, respectively. The doped-to-dedoped transition takes place at a potential of

around -0.5 V. This potential, where the resistance increases, is at a relatively more negative potential than the actual onset of HER. It might seem contradicting that an electrochemical reaction can take place at potentials where the resistance of the electrode (PEDOT) turns high. However, few factors must be taken into the account: (i) thermodynamics (Nernst equation) requires that both doped and undoped forms coexist at any potential; (ii) the electrochemical doped-to-undoped switching kinetics of conducting polymers is slow, which further increases the content of the conducting component during a cathodic potential scan ³³; (iii) PEDOT in its neutral (undoped) form is still a semiconductor that is able to transport electronic charge carriers, (iv) even non-conducting redox polymers can drive redox reactions at the solution interface ³⁴. Surprisingly, our in-situ resistometry measurement indicates that after the large increase of resistance due to the doped-to-undoped transition, we observe a partial re-doping of PEDOT when the HER takes place (Fig. S3). Although we do not understand the mechanism in details (which is beyond the scope of this article), we remind the reader that PEDOT is known to be partially doped by the action of protons ³⁵ and also that a cousin phenomenon, *i.e.* the doping of PEDOT at negative bias upon the reduction reaction of O₂ has been observed ^{36,37}.

Secondly, a negative potential generally yields the appearance of technology- and energy-relevant reactions such as oxygen reduction reaction and HER by means of heterogeneous electron transfer. The linear ramp of negative potential [0.2 V to -1.0 V] applied to the PEDOT-PEG films lead to a linear increase of recorded reduction current, typical for HER (Fig. 2B). Here, the increase of negative potential corresponds to the rise of the Fermi energy of electrons located within the electrode phase and causes a heterogeneous faradaic transfer of electrons to reduce protons, from the aqueous solution, to form molecular hydrogen. From visual inspection we also indeed observe the appearance of gas bubbles on the electrode surface (Fig. 1C). Note that the HER current level in Fig. S4A is low because of the neutral pH of the electrolyte solution; the latter was chosen to visualize the capacitive current contribution I_C of the electrode; while in Fig. 2B the faradaic HER current level is relatively much larger as promoted by an acidic electrolyte.

The soft and nano-porous character of the PEDOT-PEG film seems to have a major impact on the HER-associated currents. As consecutive voltammetry cycles are applied to the PEDOT-PEG electrode, the HER current increases by ~15 times (6th cycle) (Fig. 2C). We hypothesize that the enhancement of the voltammetric response reflects an increase of the effective surface area (porosity) which makes the electrode bulk to a greater extent participate in heterogeneous electron transfer. Further, we believe that this phenomenon, to some extent, is also assisted by that the polymer swells due to the formation of intercalated H₂ gas. This phenomenon is also accompanied by a change in the mechanism that limits the measured current, as a more negative voltage is applied; from mass transport through the film to heterogeneous electron transfer, which is evident from the plateau- and tail-shaped voltammograms, respectively (Fig. 2C). This is typical for electrochemistry performed on conducting polymer films^{17,38}. For the wide range of potentials investigated, there was no sign of limitation from mass transport on stabilized HER currents and no effect from electrolyte agitation. **Moreover, the role of the copolymer shall not be neglected. As it was reported before¹⁷, the coordination between cation species (*i.e.* proton) and PEG moiety facilitates the cationic transport and thus the proton reduction on PEDOT film.**

The role of the pH on the HER threshold potential and current density is important to measure in order to understand the **underlying** reaction mechanism and further integration to realize an electrolyzer. Polymer electrolyte membrane water electrolyzers (PEMWE) operate with pure water as medium. Going from acidic to more neutral pH does not significantly affect the electrical conductivity of the PEDOT-PEG electrode (Fig. S4B). Increasing the pH of the electrolyte implies a lower proton reactant concentration, which then results in lower HER rates (from -0.342 mA/cm² at -0.6 V, pH=0.4 to -0.015 mA/cm² at -0.6 V, pH=4.7), as illustrated in Fig. 3A. Like in all electrochemical reactions that involves protons, the redox potential is expected to depend on pH according to Nernst equation $E = E^{0'} - RT/nF \ln([H_2]/[H^+]^2)$, where E is the equilibrium potential, E^{0'} is the formal potential, R

is the gas constant, F is faraday number, n is the number of electrons transferred per each reaction event, $[H_2]$ and $[H^+]$ are the concentration of each species, respectively. Although the cyclic voltammetry is not a steady state method, we clearly observe a Nernstian shift of the threshold voltage with a slope of 47 mV/unit for PEDOT-PEG and 43 mV/unit with a Pt electrode (Fig. 3B). Moreover, the apparent onset potential of the HER at the PEDOT-PEG electrode is only shifted by 4 mV as compared to a Pt electrode, suggesting a decent overall catalytic effect. The presence of a Nernstian shift also indicates the establishment of an equilibrium between proton reduction (HER) and the hydrogen oxidation reaction (HOR) on the PEDOT surface.

The electrochemical kinetics of HER on PEDOT-PEG was evaluated by steady-state current measurements (Fig. 3C). Here, we choose to utilize a thin PEDOT-PEG film on a conducting substrate (glassy carbon electrode, GCE) since this architecture ensures that the polymer film resistance have no significant effect on the current levels recorded. Measurement of steady-state currents at different polarization states enables the monitoring of both HER- and HOR-assigned negative and positive currents, respectively. The negative polarizations are characterized by a rise of the current corresponding to HER, while the positive polarizations display a potential-independent current for the HOR. This specific and asymmetrical shape of the polarization curve manifests the involvement of a slow surface-chemical reaction. The exchange current densities of the HOR/HER equilibrium on the PEDOT-PEG films, obtained from the intercept of the extrapolated evolutions of HER and HOR currents from the Tafel regions, shows a value of $1 \times 10^{-5} \text{ A cm}^{-2}$. Surprisingly, this high value locates the rate of HER on PEDOT-PEG between the group of coinage metals (*e.g.* Ni, Co, Fe) and Au (Table 1). On top of the comparable catalytic performance, PEDOT-PEG does not suffer from chemical corrosion and passivating oxide layers in acidic media. In fact, the stability and performance of PEDOT is better in acidic media. The quantification of HER/HOR electrocatalysis on bare GCE shows values of exchange current densities of $1.4 \times 10^{-6} \text{ A cm}^{-2}$ (0.5 M H_2SO_4) and $8 \times 10^{-7} \text{ A cm}^{-2}$ (pH=3.6)

emphasizing an electrocatalytic increase of the HER process rate on PEDOT-PEG films (Fig. S5). We believe that there are three specific features explaining this remarkable high rate of HER with PEDOT-PEG, the first is an efficient catalytic effect, the second is the presence of an intrinsic molecular porosity due to the important role of van der Waals bonds in this molecular solid; the third is the absence of corrosion in acidic environment for this polymer electrode. The exchange current density shows no pH dependence, which means that the rate-determining step (RDS) is not limited by the proton concentration. High current densities obtained for PEDOT-PEG-modified GCE at negative potentials are typically characterized by mass-transport limited reactions, as indicated by the presence of clear current plateaus. The onset potential of HER, estimated from the linear plot, is *ca.* -0.37 V (Fig. S6), which is more negative than the reported values for high performance HER catalysts ³⁹. However, one should note that high performing HER catalysts are metallic and the PEDOT-PEG film is a pure organic material.

The mechanisms of heterogeneous HER (Scheme S1) commence from the reduction of a proton, then followed by the adsorption of the resulting hydrogen atom on the catalyst surface (so-called Volmer step (V)). Being decisive, the second step yields a hydrogen molecule might be either a non-electrochemical recombination of adsorbed hydrogen atoms (so-called Tafel step (T)) or a subsequent electrochemical reduction of a proton (so-called Heyrovsky step (H)). The Tafel slope for HER shows a pH-independent value of 40 mV/decade, indicating that the H-process is the RDS for HER, by the VH mechanism ⁴⁰. Note that the Tafel slope of 40 mV/decade is also reported for electrodes based on platinum in 0.5 M H₂SO₄ ⁴¹⁻⁴⁴. For a detailed investigation of the reaction mechanisms of the HER, catalyzed by PEDOT-PEG films, we explored the energetics of both pathways with the help of theoretical modeling. First, we perform quantum chemical calculations based on DFT using a minimalistic model based on single monomer approximation that provides us with free energies for the species in the gas phase and free electrons at infinity. Next, we introduce thermodynamic corrections to solvate the species and to put exchanged electrons at a chosen redox

potential, namely at 0 V (vs. RHE) in order to obtain free energy diagrams, (Fig. 4, Supporting Note 2). As a check of the precision of our procedure, we obtain overall $\Delta G = 0.18$ eV, while at this potential HER should be in thermodynamic equilibrium, $\Delta G = 0$ eV. The first step is common for both VH and VT mechanisms, then they bifurcate. The highest energy point of the VT mechanism is the transition state at 4.90 eV corresponding to the potential-independent chemical recombination (T) step. The VH mechanism passes via an H step with a potential-dependent barrier. To estimate its barrier, we consider two limiting cases: the transition state having the same charge (i) as the reactants (TS^+), with the energy of 2.35 eV and (ii) as the products (TS^0), with the energy as low as 0.04 eV. Both limiting cases of TS location are considered for non-adiabatic, instantaneous, “outer-sphere” ET, while the adiabatic ET locates the TS energetics in between of these two limits. The upper point of the H step (2.35 eV) is undoubtedly lower than the highest point of the T step (4.90 eV), which confirms the preference for the VH pathway of HER in PEDOT films.

The HER production efficiency was evaluated by *in-operando* mass spectrometry (Fig. 5A). The application of a negative potential pulse to the PEDOT-PEG electrode generates a synchronized pulse of hydrogen concentration in the gas outlet from the sealed electrolysis cell (Fig. 5B). The linear correlation between the produced hydrogen partial pressure and the applied current density (Fig. 5C) suggests a direct conversion of electrical charge into electrosynthesized hydrogen. The coulombic efficiency of the electrosynthesis is determined by the ratio between the amount of hydrogen detected, by mass spectrometry, and the amount of hydrogen expected from the consumed electric charge according to Faraday’s law. A coulombic efficiency of 40 % is here found, which is comparable to other reported electrocatalysts (Table 2), being mostly metallic catalysts since the use of organic homogeneous HER catalysts¹³ is hampered by immobilization problems. The incomplete electrical-to-chemical energy conversion might be a consequence due to hydrogen loss by leakage or by back-oxidation on the unseparated counter electrode (platinum mesh, Fig. 5A) and the presence of the

counteracting dedoping process of the organic semiconductor. The use of an insulator support^{17,18} and the absence of any iron residue-contamination, which was ensured by acid-washing and confirmed by XPS (Fig. S1), motivates us to assign the recorded production of H₂ solely to the conducting organic material.

Finally, we evaluated this conducting polymer as the cathode catalyst in a working PEMWE device (Fig. 6, Fig. S8). The steady-state polarization curve of the PEMWE, with the PEDOT-based cathode operating at 80 °C, showed a current density of 0.5 A cm⁻² at an applied voltage of 1.95 V. This is comparable with the characteristics of inorganic (platinum group metals free) PGM-free cathode catalysts (Table 3)⁴⁵⁻⁵¹. Comparing the results in the presence of PEDOT-PEG on the cathode versus the background measurement on the PEDOT-free PEMWE (*i.e.* bare porous titanium) led to a clear enhancement of HER activity. As mentioned above, a Tafel slope of 40 mV/decade for the HER, obtained in the three-electrode system setup, was reached. Same Tafel slopes, recorded from the PEDOT-PEG in the PEMWE setup, is observed only at polarizations up to 1.8 V, which illustrates that the RDS is maintained only for small current densities only. During the first runs of the PEDOT-PEG-based devices, the increase of current with applied voltage slows down at around 2.0 V but accelerates again for higher voltages. A device operated continuously for 3 days showed a relatively lower current than the bare porous titanium substrate. Both these types of loss of activity reflect a decrease in catalytic activity, under stress, that can only be due to dedoping of the conducting polymer and underscore the importance of its oxidation state for the electrocatalytic processes. Note, that the integration of PEDOT-PEG into the gas diffusion cathode was not optimized with respect to the triple phase boundary, taking the relative densities into the account, contact resistance and device operation, suggesting the possibility for considerable improvement of performance.

Conclusions

To conclude, for the first time, the semiconductor behavior of PEDOT, while composited with PEG, leads to a true all-organic polymer electrocatalyst system for HER with efficient electrical-to-chemical energy conversion and good stability (neither oxide film formation nor chemical corrosion) in acidic media. We believe that this might be extrapolated to other non-metallic organic electrocatalysts and that a molecular design of the catalytic activity can be further explored. The consistency between results gained from electrochemical, computational and physical methods encourage us to quantify the classical model reaction for HER (Volmer-Heyrovsky mechanism) on the organic catalyst, from mechanistic aspects to the operation of a first electrolyzer using an organic electrode for H₂ production.

The cost of catalysts being the key limitation of the establishment of a large-scale hydrogen economy, an organic catalyst represents an attractive candidate, in part owing to a low-temperature synthesis protocol including earth-abundant elements and easy processing and manufacturing. Moreover, printing technologies can be used to pattern coatings of those electrocatalytic polymers on large area at low-cost and high manufacturing rate. This is a breakthrough for the H₂-technology production and opens a way for large-area organic electrolyzers for the mass production of H₂, targeting energy storage and conversion by fuel cells for cities.

Experimental section

Reagents

All inorganic salts, hydrochloric acid, ethanol, isopropanol, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG, 5800 g mol⁻¹) and 3,4-ethylenedioxythiophene (EDOT) were purchased from Sigma (Sweden) and used as received. Iron (III) OTf (90 %) was purchased from Alfa Aesar and used as received. Iridium (II) oxide (IrO₂) and platinum nanoparticles supported on Vulcan XC-72 carbon black (Pt/C) were purchased from Fuel Cell Store Inc. Experiments were carried out with deionized water.

Procedures

The PEDOT-PEG film was prepared by vapor phase polymerization (VPP)⁵². The oxidant solution containing 3 wt % Fe(OTf)₃ and 20 wt % triblock copolymer PEG-PPG-PEG was spin coated on a clean glass substrate (Thermo Scientific) at 3000 rpm for 30 s. Thereafter, the substrate was heated up to 70 °C on a hot plate for 30 s to evaporate the solvent. Afterwards, the substrate was placed in a vacuum chamber (JP Selecta, 70 mbar) containing EDOT at 30 °C for a desired polymerization time (*e.g.* 1 h). Then, the substrate was placed again on a hot plate at 70 °C for 2 min to complete the polymerization. Finally, the sample was sequentially washed by ethanol, 20 v % HCl -in order to remove the iron residues-, deionized water and dried in air.

Methods

Electrochemical measurements were performed in a three-electrode setup in a sealed cell with a BioLogic SP200 potentiostat with a platinum mesh (25×35 mm) and a Ag/AgCl electrode in 3.0 M NaCl as counter and reference electrodes, respectively. The absence of platinum counter electrode dissolution⁵³ was confirmed by the electrochemical measurements with the large glassy carbon counter electrode (Fig. S9). *In-situ* resistometry was done using a customized gold interdigitated microband electrode (Micrux Technologies) with an Autolab type III bi-potentiostat (Metrohm-Autolab) with a platinum mesh (25×35 mm) and Ag/AgCl electrode in 3.0 M NaCl as counter and reference electrodes, respectively. The measurement in the aprotic electrolyte using 0.1 M tetraethylammonium hexafluorophosphate (TEAP, 99%, Sigma Aldrich) in anhydrous acetonitrile (CAN, Sigma Aldrich) was performed under inert gas conditions in a glove box. A Pt quasi-reference electrode was employed, which was calibrated by the ferrocene peak (Fig. S10). Four-point probe conductivity measurement was done by using a sourcemeter (Keithley 2400) as reported before²⁶. Steady-state polarization measurements were performed on GCE rotating disk electrode (5 mm

diameter, Pine Research Instrumentation Inc.). Prior to use, GCE was successively polished with 1.0 and 0.05 μm Al_2O_3 powders and sonicated in Milli-Q water. Prior to all electrochemical measurements, the cell with electrolyte was thoroughly purged by nitrogen for 20 min. *In-operando* mass spectrometry studies were done in a sealed electrochemical cell (Fig. 5A) using a constant nitrogen flow (30 mL min^{-1}) with a hydrogen-calibrated HPR 20 Hiden mass spectrometer (Hiden Analytical) in combination with an Autolab type III potentiostat (Metrohm-Autolab).

The PEMWE was assembled with PEDOT-PEG as a cathode catalyst. The Membrane-electrode assembly (MEA) was elaborated on a Nafion® 117 polymer electrolyte membrane (Du Pont) and porous titanium disks (30% porosity, 900 μm thickness) as gas diffusion electrodes (GDE)⁵⁴ coated with catalytic layers. IrO_2 ⁵⁵ and Pt/C^{56,57} were used as anode and reference cathode catalysts, respectively. The catalyst and 5 wt % Nafion® solution (Du Pont) were homogenized in isopropanol using an ultrasonic bath with the working frequency of 22-25 kHz. The resulting catalyst ink was air sprayed onto GDEs surface with 2 mg cm^{-2} loading. PEDOT-PEG was loaded on GDEs by VPP as described previously. The polymer electrolyte membrane was sandwiched between catalyst coated GDEs to form the MEA, which was evaluated in a PEM water electrolyzer consisting of two thermostatic half-cells with a working surface area of 7 cm^2 ⁵⁸. All water electrolysis measurements were performed at a temperature of 80 °C.

Film thickness and morphology were studied by atomic force microscopy (AFM, Veeco-Dimension 3100). X-ray photoelectron spectroscopy (XPS) was done on an XPS spectrometer (Scienta ESCA 200).

Supporting Information

Supporting Information is available in another file.

Acknowledgements

This study was financially supported by Göran Gustafssons Stiftelse (no. 25034 300523), the Knut Alice Wallenberg Foundation (WWSC), the Peter Wallenberg Foundation (Grant PWS-2016-0010), Vetenskapsrådet (paper fuel cell), National Research Centre “Kurchatov Institute” (directive No 1808 from 14.08.2019, subprogram 6), and the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No. 2009-00971). The computations were performed on resources provided by the Swedish National Infrastructure for Computing (SNIC) at NSC and HPC2N. Robert Brooke is acknowledged for his great help and fruitful discussions for the polymer preparation.

Competing interests

The authors declare no competing interests.

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Table 1. Exchange current densities of HER on coinage group metals.

Electrocatalyst	Exchange current density, $\times 10^{-6} \text{ A cm}^{-2}$	Reference
Gold	26	59
	29	60
Pt	800	61
PEDOT	10	Present work
Nickel	6.2	62
Cobalt	4.8	62
Copper	4.3	62
	3	63
	0.14	59
Iron	0.57	59

Table 2. Coulombic efficiency for HER on different electrocatalysts.

Electrocatalyst	Coulombic efficiency	Reference
PEDOT	<i>ca.</i> 40%	Present work
PANI/MWCNTs	47.2%	64
CoMoS₄ nanosheets	<i>ca.</i> 100%	65
Carbon cloth containing Pt	69.3%	66
Ru⁰/CeO₂	<i>ca.</i> 100%	67

Table 3. Performance characteristics of different PEMWE based on PGM-free cathodes.

Cathode catalyst	Operational temperature, °C	Nafion thickness, μm	Overpotential at 0.5 A cm^{-2} , V	Reference
PEDOT	80	183	1.95	Present work
$\text{Fe}(\text{Cl}_2\text{Gm})_3(\text{BC}_6\text{H}_5)_2$	80	183	1.95	49
$\text{Fe}((\text{Phen}(\text{CH}_2)_3\text{S})_2\text{Gm})_3(\text{Bn}-\text{C}_4\text{H}_9)_2$	80	183	1.99	68
MoS_2 on Vulcan	80	183	2.0	51
MoS_x on carbon black	80	127	1.85	47
Mo_3S_{17} on carbon black	80	127	1.8	47
FeS2 on carbon	80	127	2.0	50
$\text{Cu}_{93.7}\text{Mo}_{6.3}$	90	50.8	1.9	48
MoS_x on carbon paper	90	50.8	1.95	46
$\text{Ni}_{0.64}\text{Co}_{0.36}\text{O}_x\text{S}_{0.14}$	90	50.8	1.97	45

Figure 1.A: Chemical formula of PEDOT, OTf and the copolymer PEG-PPG-PEG abbreviated “PEG” in this article. **-B:** - AFM micrograph of PEDOT-PEG film (phase and topography image). **C:** Photograph of electrosynthesized hydrogen bubbles on PEDOT-PEG.

Figure 2. Decoupling of interior and heterogeneous electron transfer on semiconducting catalyst. Resistometry was performed on PEDOT-PEG-modified electrodes in nitrogen-saturated neutral (1.0 M KCl), acidic ($0.5 \text{ M H}_2\text{SO}_4$) and aprotic (0.1 M TEAP in ACN) electrolytes (A). The resistance is normalized to 1 at a potential of $+1.0 \text{ V}$. Cyclic voltammetry was measured in 1.0 M KCl (B) and $0.5 \text{ M H}_2\text{SO}_4$ (C) electrolytes (scan rate 5 mV s^{-1}). The bright blue dashed line in (B) is representing the cyclic voltammogram on the bare glass substrate.

Figure 3. pH effect on HER. **A:** Cyclic voltammograms obtained for PEDOT-PEG electrodes in nitrogen-saturated 0.5 M H_2SO_4 solution with different pH values adjusted by NaOH; scan rate 5 mV s^{-1}); **B:** pH dependences of apparent HER onset potential for PEDOT-PEG and platinum. **C:** IR-

compensated steady-state polarization curves obtained on PEDOT-PEG-modified GCE (rotating disk electrode, 900 rpm,) in electrolytes (0.5 M H₂SO₄) of different pH values adjusted by NaOH (pH 0.4, 1.1, 2.1, 3.6 as red, green, blue and magenta symbols, respectively; oxidation and reduction currents as open and filled symbols, respectively).

Figure 4. Free energy diagrams for the HER on PEDOT-PEG: the Volmer-Tafel mechanism (Red) and the Volmer-Heyrovsky mechanism (Green).

Figure 5. The efficiency of electrical-to-chemical conversion by HER on PEDOT-PEG films. **A:** Schematic diagram of the *in-operando* mass spectrometry setup. **B:** the dynamics of hydrogen production upon applied potential pulse (-1.27 V vs RHE); **C:** the dependence of partial pressure of electrosynthesized hydrogen on current density.

Figure 6. Performance of a PEMWE with the PEDOT-based cathode. The steady-state polarization curves obtained on bare (□) and PEDOT-PEG- (■) or Pt/C-modified (■) cathodes of PEMWE (Nafion 117; IrO₂-based anode; 80 °C). The blue arrow shows the direction from 1st to 3rd day.

Supporting Information

Electrochemical hydrogen production on a metal-free polymer

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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.

In-situ conductivity calculations

For the *in-situ* conductivity measurements of the electroactive polymer, we employed a setup originating from the works of Wrighton's group^{1,2}. The polymer is electrodeposited, while for our work via vapor phase polymerization (VPP), onto two interdigitated working electrodes (WE I and WE II) that can be polarized independently by a bipotentiostat. During linear potential sweep, a small bias between WE I and WE II, $\Delta E = E_{II} - E_I$ (typically $\Delta E = +50$ mV in this work) is maintained. The resistance, the inverse of conductivity, of the polymer film between the electrodes, R_p , is evaluated as $R_p = \Delta E / i_p$ where i_p is the channel current between WE I and WE II. However, this channel current is not directly measurable, so its evaluation requires some sort of model. In spite of wide applicability of this approach, there is surprisingly little discussion of the adopted approximations. A notable exception is the work from the Uppsala group³, in which an explicit analysis is presented. Our analysis is largely based on this work, but our conclusions are somewhat different. The specific resistance can be determined by normalizing to the film thickness.

In the context of this study, two very different regimes of *in-situ* conductivity measurement are swept: (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.

The circuit analysis from Ref.³ yields for the channel current:

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

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 faradaic currents at these electrodes, unmeasurable in the presence of the channel current. The working formula used in that work to calculate the channel current is:

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

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

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

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

$$i_0^I = i_{F0}^I, i_0^{II} = i_{F0}^{II}. \quad (3)$$

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

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

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

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

$$i^{II} + i^I = i_F^{II} + i_F^I \quad (5)$$

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

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

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

$$i_p = i_0^I - i^I \quad (7)$$

which is the formula used to calculate the resistance of the polymer in this work.

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 M H_2SO_4 , 5 mV s^{-1} , 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^{-1}). **(B)** *In-situ* resistometry were performed on PEDOT-PEG-modified interdigitated electrodes in nitrogen-saturated 1.0 M KCl or 0.5 M H_2SO_4 (black or red curves, respectively; scan rate 5 mV s^{-1}).

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 H₂SO₄; oxidation and reduction currents as open and filled symbols, respectively).

Figure S6. HER electrocatalysis on PEDOT-PEG. IR-compensated steady-state polarization curve obtained on PEDOT-PEG-modified GCE (rotating disk electrode, 900 rpm; 0.5 M H_2SO_4).

Figure S7. Free energy profiles for the HER on PEDOT for the Volmer-Tafel mechanism (Red) and the Volmer-Heyrovsky mechanism (Green) as obtained from Gaussian calculations with gas phase thermochemical corrections.

Supporting Note 2.

Quantum chemical calculations

Path1. Volmer-Tafel Mechanism	Path2. Volmer-Heyrovsky Mechanism
Step 1 – Volmer step 1 (1-V) $\boxed{\text{PEDOT}^0} + 2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow \boxed{\text{PEDOT}^0}\text{-H} + \text{H}_2\text{O} + \text{H}_3\text{O}^+ + \text{e}^-$	Step 1 – Volmer step 1 (1-V) $\boxed{\text{PEDOT}^0} + 2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow \boxed{\text{PEDOT}^0}\text{-H} + \text{H}_2\text{O} + \text{H}_3\text{O}^+ + \text{e}^-$
Step 2 – Volmer step 2 (2-V) $\boxed{\text{PEDOT}^0}\text{-H} + \text{H}_2\text{O} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H-}\boxed{\text{PEDOT}^0}\text{-H} + 2\text{H}_2\text{O}$	Step 2 – Heyrovsky step (2-H) $\boxed{\text{PEDOT}^0}\text{-H} + \text{H}_2\text{O} + \text{H}_3\text{O}^+ + \text{e}^- \rightarrow \boxed{\text{PEDOT}^0} + \text{H}_2 + 2\text{H}_2\text{O}$
Step 3 – Tafel step (3-T) $\text{H-}\boxed{\text{PEDOT}^0}\text{-H} + 2\text{H}_2\text{O} \rightarrow \boxed{\text{PEDOT}^0} + \text{H}_2 + 2\text{H}_2\text{O}$	
Overall: $\boxed{\text{PEDOT}^0} + 2\text{H}_3\text{O}^+ + 2\text{e}^- \rightarrow \boxed{\text{PEDOT}^0} + \text{H}_2 + 2\text{H}_2\text{O}$	

Scheme S1. Reactions steps of heterogeneous HER

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

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.

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

Reference data

1. Hydrogen atom ionization: 13.60 eV ⁸

2. Hydrogen molecule dissociation: 4.48 eV

$$36\,118.0\text{ cm}^{-1} = 36118.0/8065.5\text{ eV} = 4.48\text{ eV}^9$$

3. Proton hydration: -11.39 eV ¹⁰

$$\Delta G_{\text{hyd}298}(\text{H}^+) = -262.4 \text{ kcal/mol} = -11.39 \text{ eV}$$

4. Proton affinity of H_2O : -7.18 eV ¹¹

5. Water molar free energy of vaporization: 0.10 eV

Water molar enthalpy of vaporization:

$$45.051 \text{ kJ mol}^{-1} (0 \text{ }^\circ\text{C}), 40.657 \text{ kJ mol}^{-1} (100 \text{ }^\circ\text{C})$$

extrapolated to $43.952 \text{ kJ mol}^{-1} = 0.46 \text{ eV}$ ($25 \text{ }^\circ\text{C}$) ¹²:

$$\text{As at } 100 \text{ }^\circ\text{C}, \Delta G_{\text{vap}} = \Delta H_{\text{vap}} - T\Delta S_{\text{vap}} = 0,$$

$$\Delta S_{\text{vap}} = \Delta H_{\text{vap}} / T = 0.4555 \text{ eV} / 373 \text{ K} = 1.22 * 10^{-3} \text{ eV/K}, \text{ weakly dependent on } T.$$

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

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.

Therefore, the reaction $2\text{H}_3\text{O}^+_{(\text{g})} + 2\text{e}_{(\text{inf})} \rightarrow 2\text{H}_2\text{O}_{(\text{g})} + \text{H}_{2(\text{g})}$ can be replaced by the following sequence, with the free energies from the Reference data above:

where (g) stands for the gas phase, and the energy of electrons at infinity, $\text{e}_{(\text{inf})}$, is zero. This value is to be compared to the free energy change from reactants to the final products from the Gaussian

calculations, which is -17.12 eV. Note that PEDOT does not intervene in the free energy calculations because it returns to initial state at the end of the cycle, as a catalyst should do. Our gas phase free energy change is therefore in excellent agreement with independent thermodynamic data. However, electrochemical conditions in aqueous solution are very different energetically.

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

i) From electrons at infinity to electrons at a chosen electrochemical (redox) potential vs. a reference electrode, ii) From gas phase to aqueous solution.

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

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:

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

This reaction has a positive ΔG , 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:

Note that the IUPAC reference value is -4.44 eV^{12} confirming the exactness of our thermodynamic approach. This means that in order to construct free energy diagrams at 0 V vs. SHE, -4.45 eV per free electron should be added when calculating the free energy balance. Solvation free energy of H_3O^+ :

$\text{H}_3\text{O}^+_{(\text{g})} \rightarrow \text{H}_3\text{O}^+_{(\text{s})}$ can be replaced by the sequence:

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 Gaussian free energies, we need to add the following stabilization (negative) energy terms:

$$\text{for each free electron:} \quad \Delta E_{\text{e}} = -4.45 \text{ eV}$$

$$\text{for each } \text{H}_3\text{O}^+: \quad \Delta E_{\text{H}_3\text{O}^+} = -4.31 \text{ eV}$$

$$\text{for each } \text{H}_2\text{O}: \quad \Delta E_{\text{H}_2\text{O}} = -0.10 \text{ eV}$$

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

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

The free DFT energy calculation in the gas phase for this step gives $E_{\text{DFT}} = -7.83$ 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 $\Delta E = -\Delta E_{\text{e}} - \Delta E_{\text{H}_3\text{O}^+} + \Delta E_{\text{H}_2\text{O}} = +4.45 + 4.31 - 0.10 = 8.66$ eV, which results in the free energy $E = -7.83 + 8.66 = 0.83$ (eV) for the aqueous phase and free electrons from SHE.

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

	VH gas inf	VH aq SHE		VT gas inf	VT aq SHE
$\text{PEDOT}^0 + 2\text{H}_3\text{O}^+ + 2\text{e}^-$	0.0	0.0	$\text{PEDOT}^0 + 2\text{H}_3\text{O}^+ + 2\text{e}^-$	0.0	0.0
$\text{PEDOT}^0\text{-H} + \text{H}_2\text{O} + \text{H}_3\text{O}^+ + \text{e}^-$	-7.83	0.83	$\text{PEDOT}^0\text{-H} + \text{H}_2\text{O} + \text{H}_3\text{O}^+ + \text{e}^-$	-7.83	0.83
			$\text{H-PEDOT}^0\text{-H} + 2\text{H}_2\text{O}$	-15.97	1.35
$\text{PEDOT}\dots\text{H}\dots\text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{e}^-$ (TS+)	-6.31	2.35	$\text{H}\dots\text{PEDOT}^0\dots\text{H} + 2\text{H}_2\text{O}$ (TS)	-12.42	4.90
$\text{PEDOT}\dots\text{H}\dots\text{H}_3\text{O}^0 + \text{H}_2\text{O} + \text{e}^-$ (TS0)	-13.15	0.04			
$\text{PEDOT}^0 + \text{H}_2 + 2\text{H}_2\text{O}$	-17.14	0.18	$\text{PEDOT}^0 + \text{H}_2 + 2\text{H}_2\text{O}$	-17.12	0.20

“gas inf” means molecules in the gas phase, free electrons at infinity, “aq SHE” means molecules in aqueous phase, free electrons at the Standard Hydrogen Electrode free energy.

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® membrane; 5 – current collectors/gas diffusion electrodes (porous titanium discs); 6 – sealants; 7 – electrocatalytic layers.

Figure S9. Cyclic voltammograms obtained for PEDOT-PEG electrode in nitrogen-saturated 0.5 M H_2SO_4 with a glassy carbon counter electrode. Scan rate 5 mV s^{-1} .

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^{-1}). The measurement was performed in a glovebox under inert conditions.

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