Electrochemical hydrogen production on a metal-free polymer

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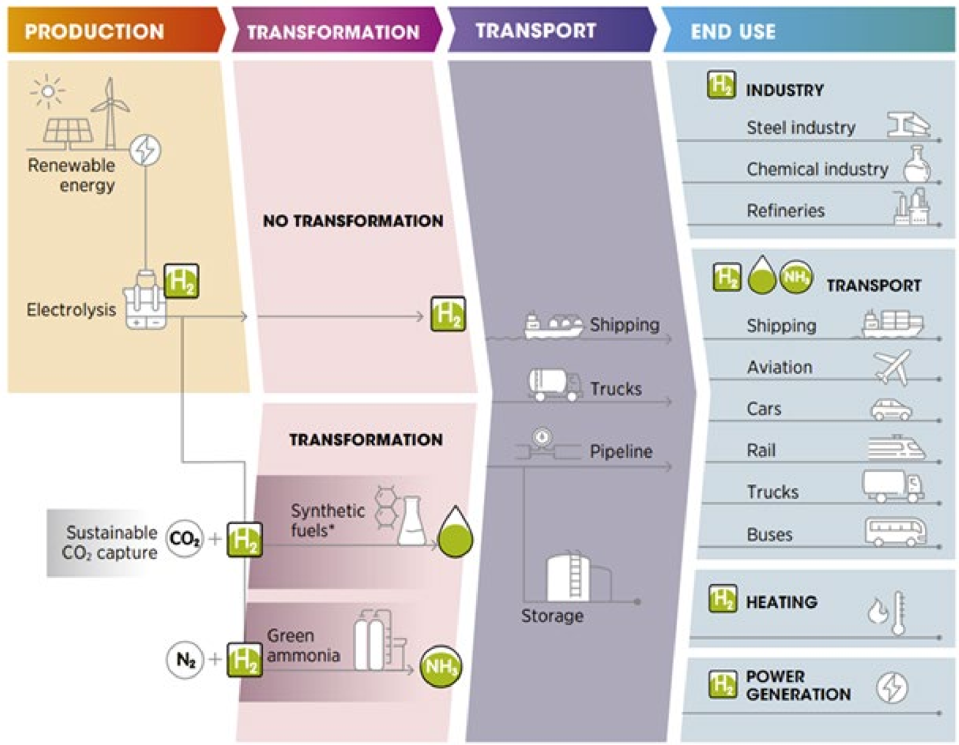
19. April 2023

• What is hydrogen needed for?



Source: IRENA.

** The term synthetic fuels refers here to a range of hydrogen-based fuels produced through chemical processes with a carbon source (CO and CO_2 captured from emission streams, biogenic sources or directly from the air). They include methanol, jet fuels, methane and other hydrocarbons. The main advantage of these fuels is that they can be used to replace their fossil fuel-based counterparts and in many cases be used as direct replacements – that is, as drop-in fuels. Synthetic fuels produce carbon emissions when combusted, but if their production process consumes the same amount of CO_2, in principle it allows them to have net-zero carbon emissions.*

In 2021, **Toyota** sold more than 2,600 Mirais in the US.

"Mirai" means "future" in Japanese

- A HYDROGEN TRUCK FROM RETRALOG AG DRIVES ON SWISS ROADS FOR **SWISS POST.**

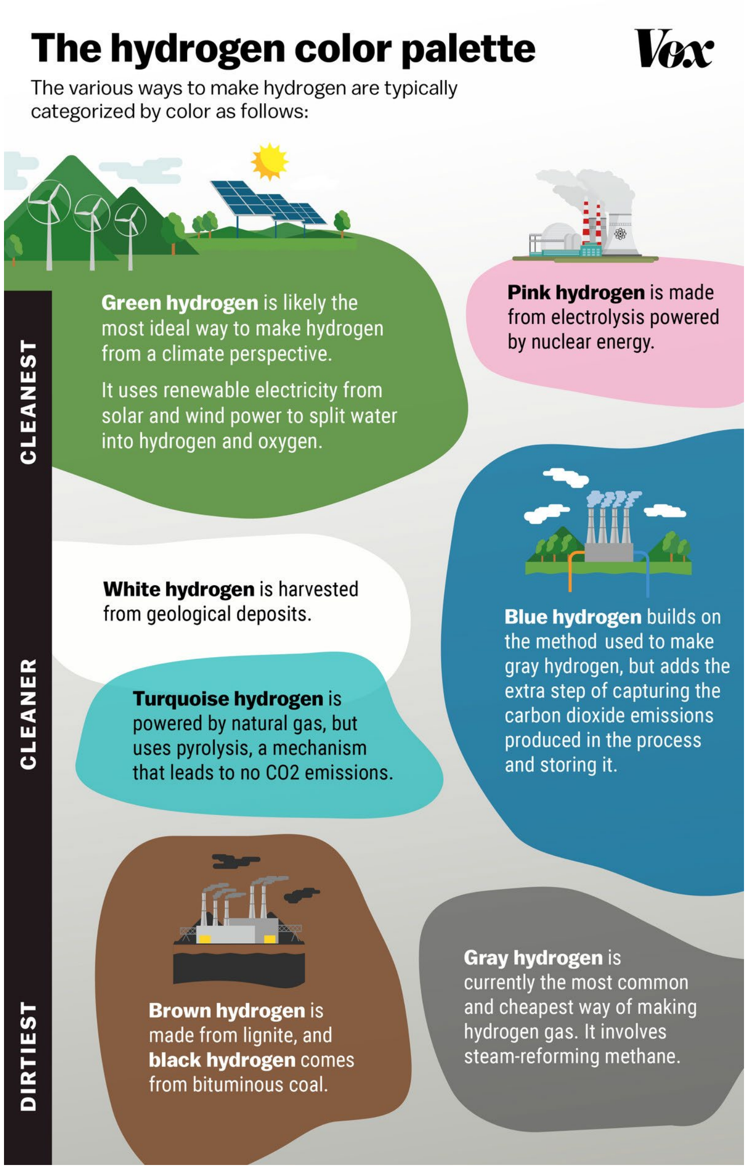
- **Delta Airlines and Airbus** signed an agreement to develop hydrogen-powered aircraft.

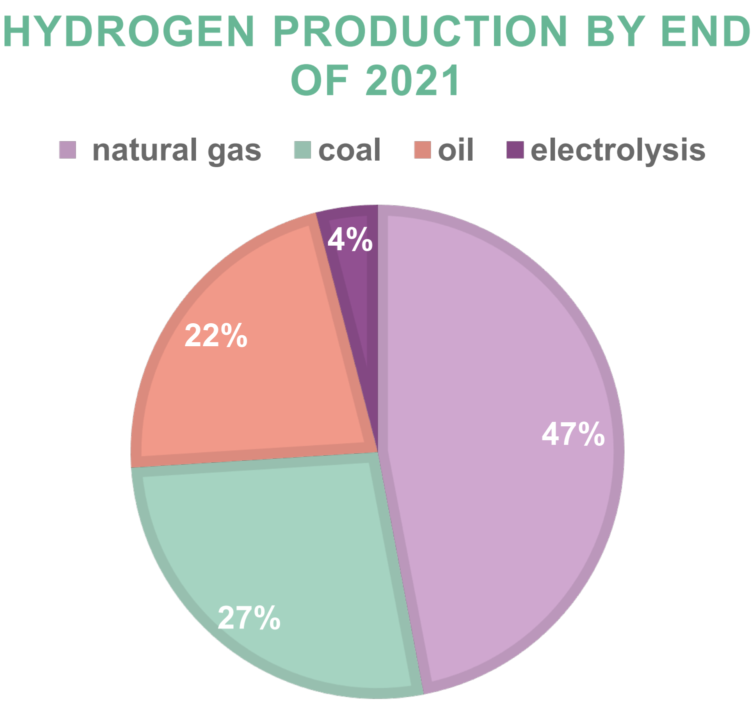
AIRBUS

- **China announced plans to produce as much as 200,000 tons of carbon-free hydrogen per year to help run a fleet of 50,000 fuel cell-powered vehicles by 2025.**

- The United Kingdom is aiming to **double** its hydrogen production.

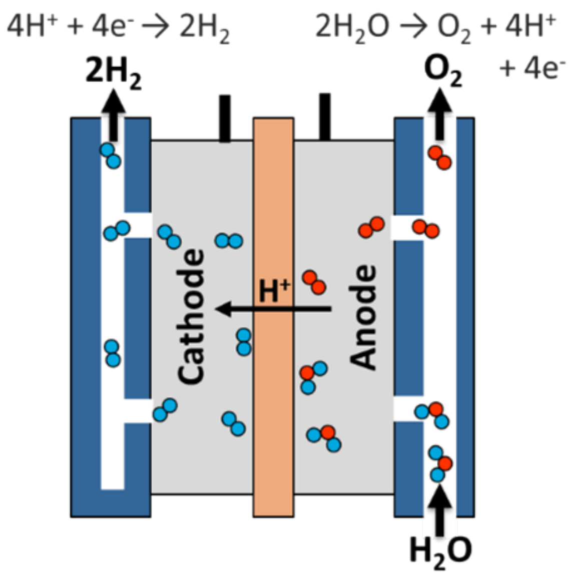
• Hydrogen production



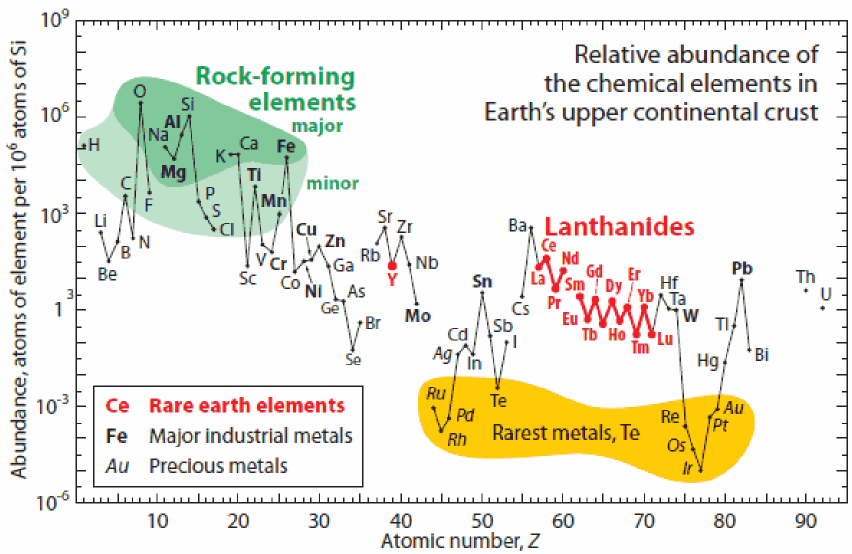


Production of hydrogen - U.S. Energy Information Administration (EIA)
Does hydrogen have any hope as a clean fuel? - Vox

• Hydrogen production



Hydrogen production via water splitting



- Platinum and Iridium are usually used as catalyst for hydrogen production via electrolysis.
- These elements are rare and expensive.

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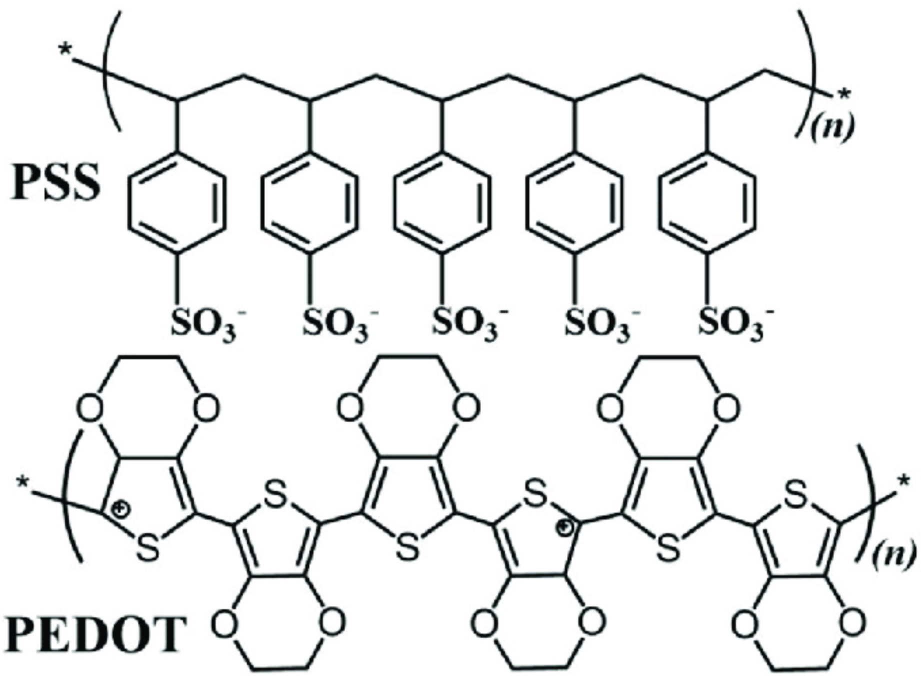
- **Poly(3,4-ethylenedioxythiophene): PEDOT**

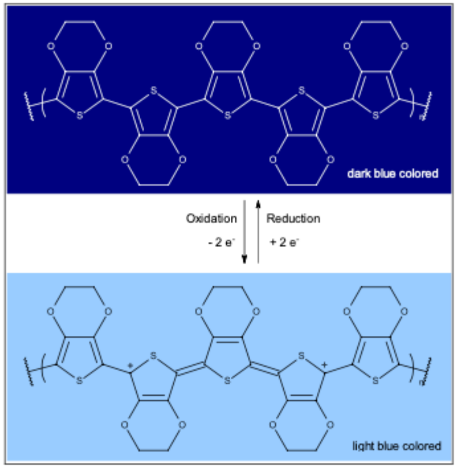
- IUPAC name: poly(2,3-dihydrothieno[3,4-*b*][1,4]dioxane-5,7-diyl))
- It is a conducting polymer based on 3,4 ethylenedioxythiophene or EDOT.
- It was first reported by Bayer AG in 1989.

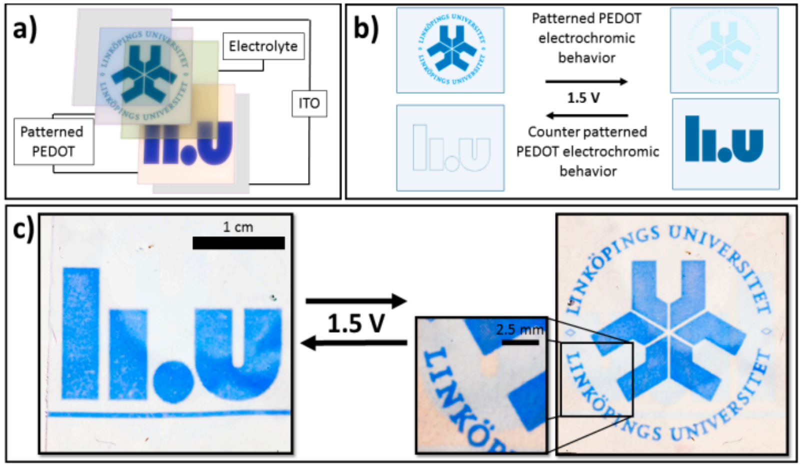


L. Zhang, et. al., 6 (2019) Adv. Electron. Mater. 6. 1900648-1900656.

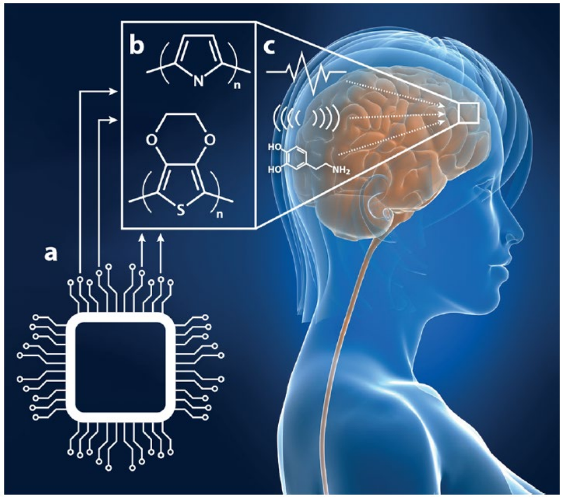
• PEDOT: applications field

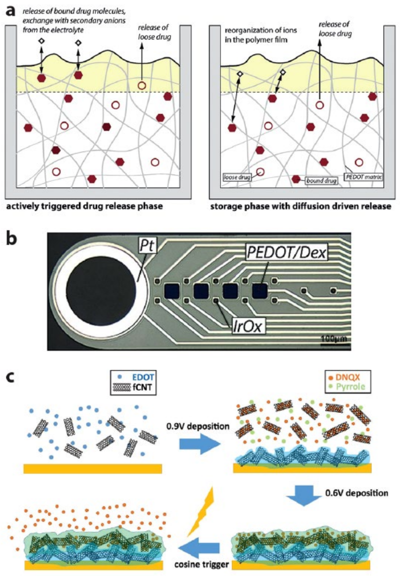
- Touch screen: because its oxidized and reduced form have different colors





- Organic Bioelectronics and controlled drug delivery
  - PEDOT is a biocompatible polymer

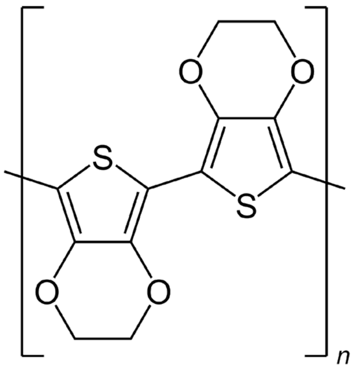




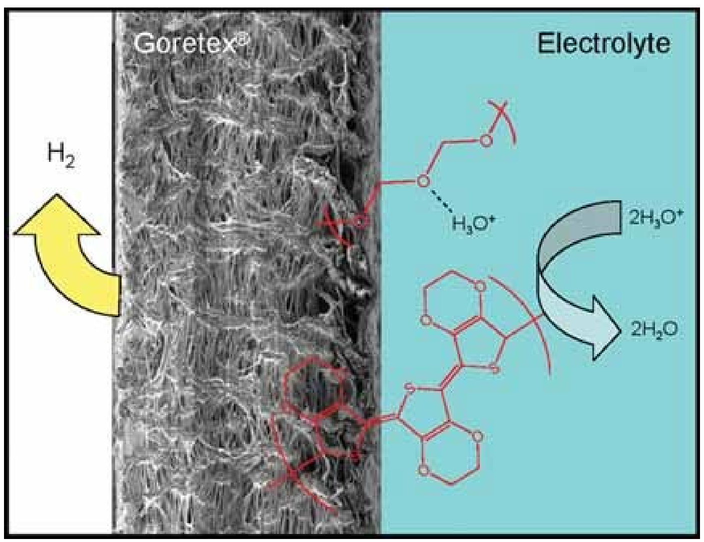
R. Brooke, et. al., Polymers 11 (2019) 267-276
M. Berggren, et. al., Chem. Rev. 2022, 122, 4826−4846

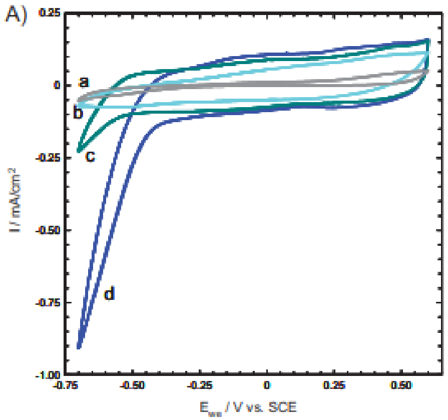
Why PEDOT for Hydrogen production?

- Chemical stability and high electrical conductivity
- Low temperature synthesis
- Easy and different methods to synthesize
- Favorable electrochemical and electric properties in acidic solutions
- Low price



PEDOT





PEDOT was already studied for hydrogen evolution reaction (HER) but there was a debate, if it comes from PEDOT or the underneath Ti substrate!

R.Valiollahi, et. al., Sustainable Energy Fuels 3 (2019) 3387–3398
B. Winther-Jensen, et. Al., Adv. Mater. 22 (2010) 1727-1730.

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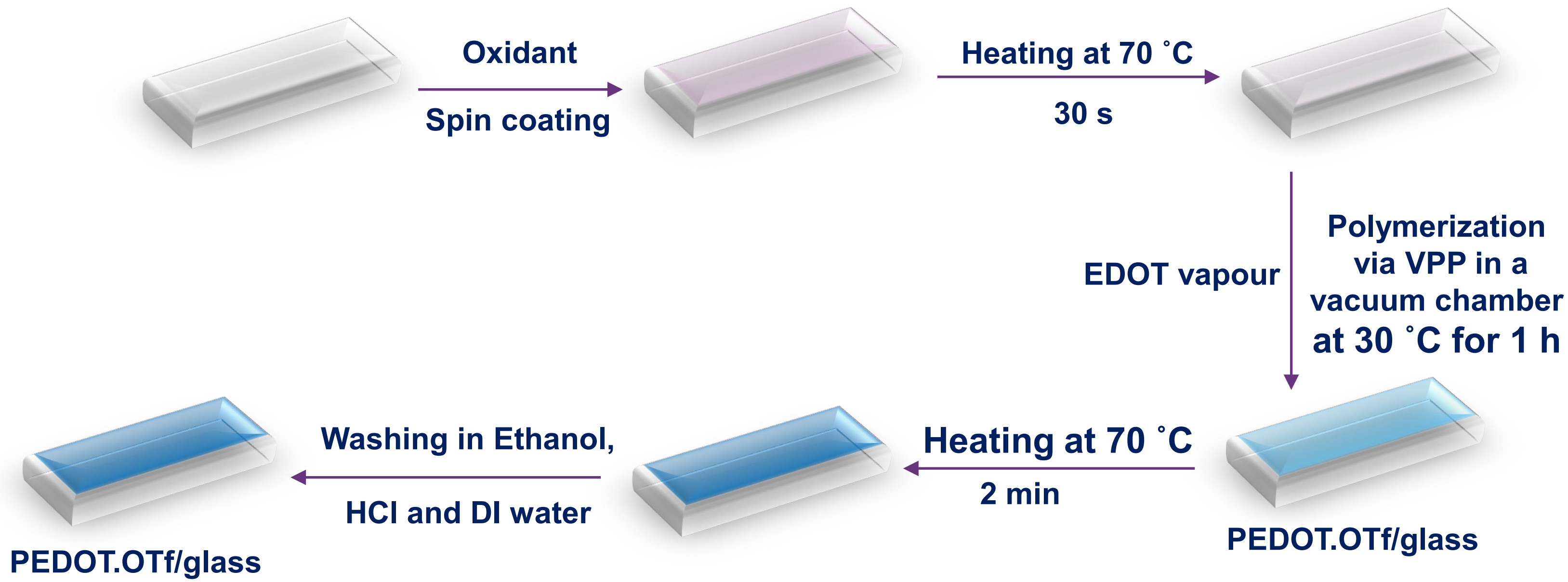
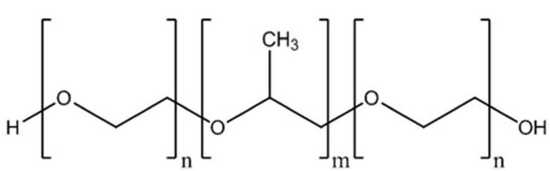
• Electrode preparation

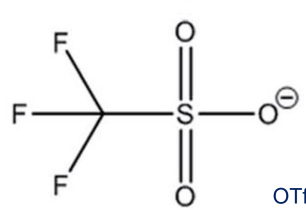


PEG-PPG-PEG

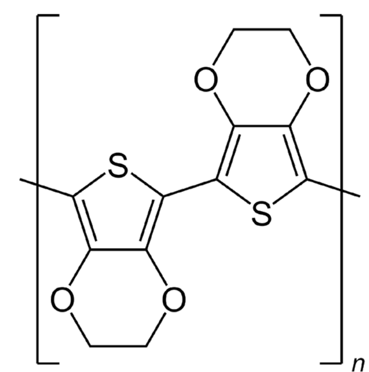


Poly-(ethylenglykol)-block-poly-(propylenglykol)-block-poly-(ethylenglykol)

OTf



Oxidant: Iron (III).OTf
OTf: Trifluoromethanesulfonate



PEDOT

R.Valiollahi, et. al., Sustainable Energy Fuels 3 (2019) 3387–3398

• Electrochemical characterization

$PEDOT^+Cl^- + e^- \rightarrow PEDOT^0 + Cl^-$

$PEDOT^0 + 2H_3O^+ + 2e^- \rightarrow PEDOT^0 + H_2 + 2H_2O$

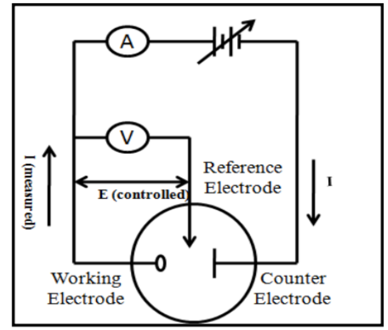


Figure 2.A simplified circuit for cyclic voltammetry Set Up.

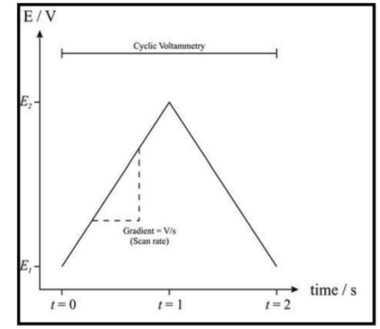
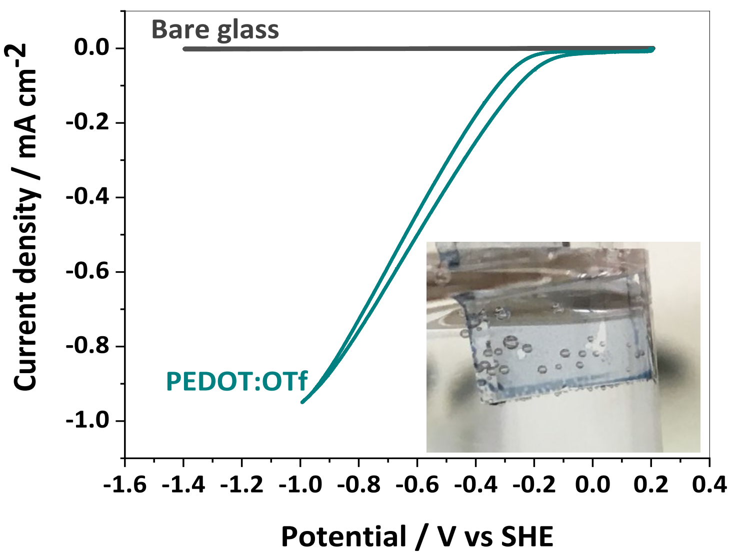
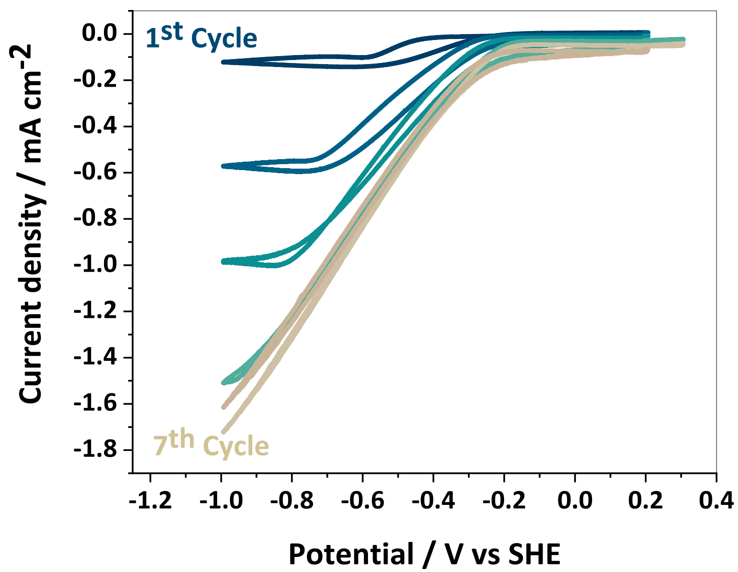


Figure 3.Cyclic voltammetry Potential waveform.



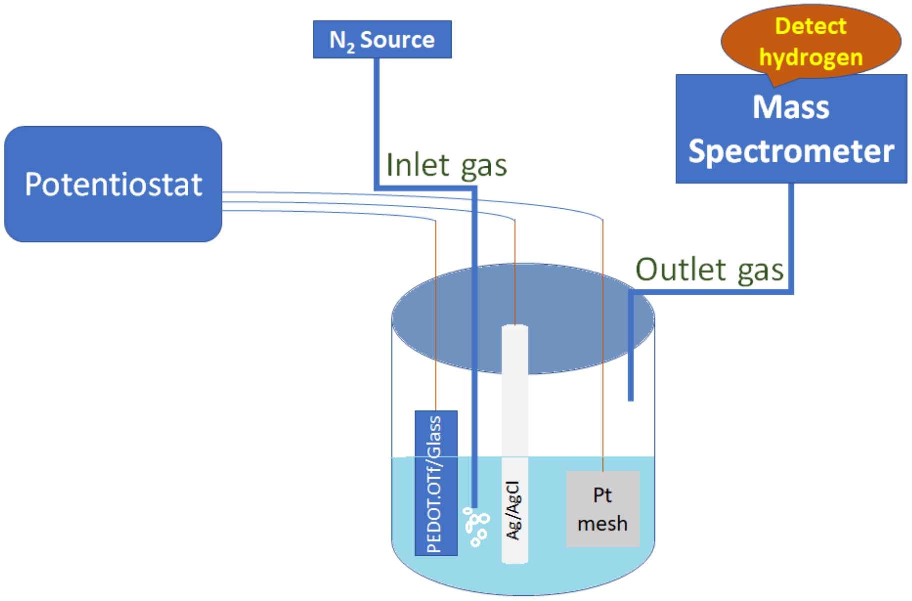


Cyclic voltammetry of PEDOT/glass in 0.5 M H_2SO_4, scan rate: 5 mV s^{-1}

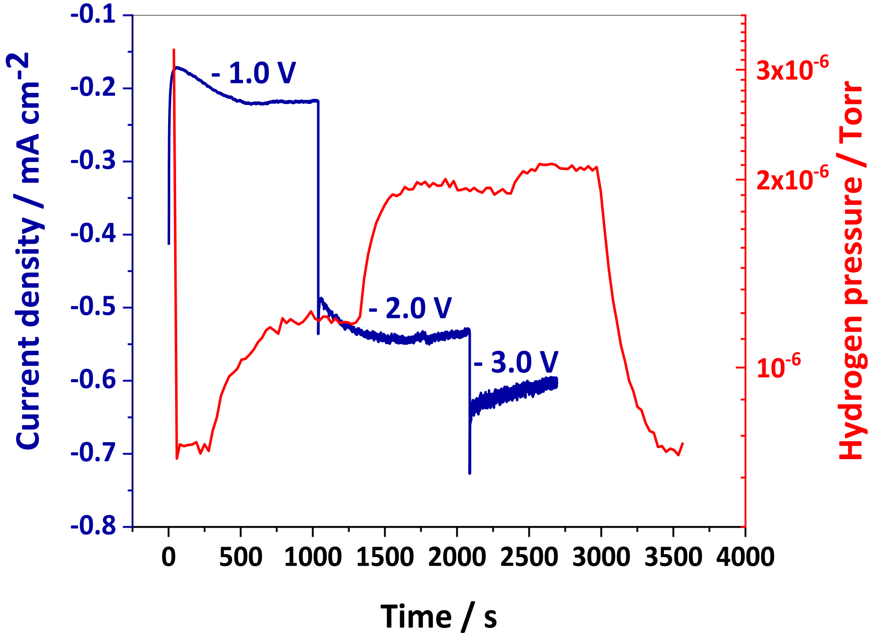
❖ PEDOT is activated by electrochemical cycling, which leads to a film swelling and facilitates proton diffusion through the film.

R.Valiollahi, et. al., Sustainable Energy Fuels 3 (2019) 3387–3398
P.S. Joshi et. al., Int. J. ChemTech Res., 11 (2018) 77-88

• *Online* mass spectrometry



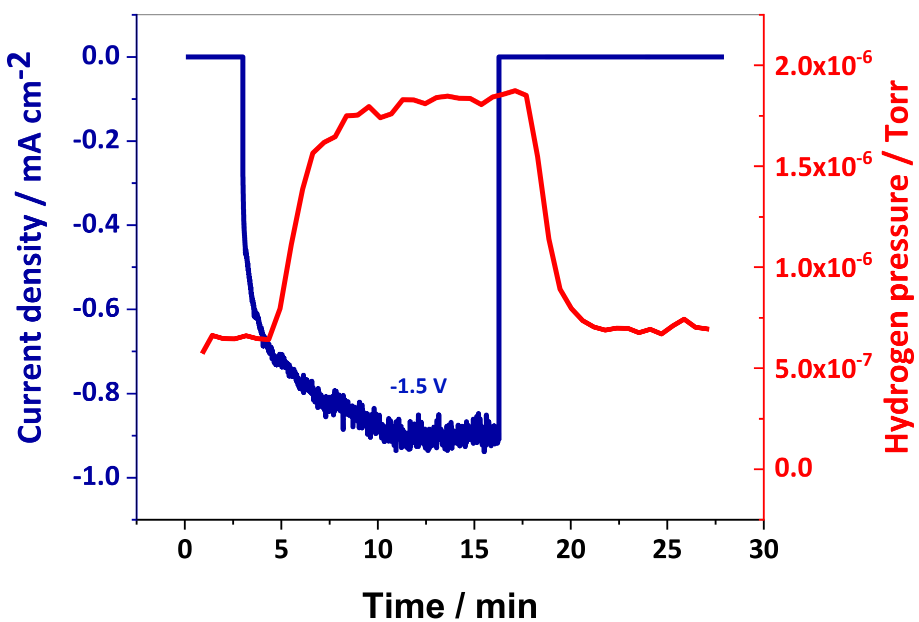
constant nitrogen flow (30 mL/min) with a hydrogen calibrated mass spectrometer in combination with a potentiostat



Three different potentials were applied and the hydrogen pressure was measured.

R.Valiollahi, et. al., Sustainable Energy Fuels 3 (2019) 3387–3398

• Coulombic efficiency measurement



Electrocatalyst	Coulombic efficiency	Reference
PANI/MWCNTs	47.2%	1
$CoMoS_4$ nanosheets	ca. 100%	2
Carbon cloth containing Pt*	69.3%	3
Ru^0/CeO_2	ca. 100%	4
PEDOT.OTf	ca. 40%	5

*In a single-chamber membrane-less microbial electrolysis cell

Coulombic efficiency: *ca.* 40%

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.

1.Qian Yang, et. al., J. Chem. Technol. Biotechnol. 90 (2015) 1263-1269
2.Xiang Ren, et. al., Nano Res. 11 (2018) 2024-2033
3.Yejie Ye, et. al., Water Sci. Tech. 61 (2010) 721-727
4.Elif Demir, et. al., Appl. Mater. Interfaces 10 (2018) 6299-6308
5. R. Valiollahi, et. al., Sustain. Energy Fuels 3 (2019) 3387-3398

Mechanism study with Density Functional Theory (DFT) calculations

Quantum chemical calculations

Path1. Volmer-Tafel Mechanism	Path2. Volmer-Heyrovsky Mechanism
Step 1 – Volmer step 1 (1-V) [PEDOT^0] + $2H_3O^+$ + 2e → [PEDOT^0]–H + H_2O + H_3O^+ + e	Step 1 – Volmer step 1 (1-V) [PEDOT^0] + $2H_3O^+$ + 2e → [PEDOT^0]–H + H_2O+ H_3O^+ + e
Step 2 – Volmer step 2 (2-V) [PEDOT^0]–H + H_2O + H_3O^+ + e → H–[PEDOT^0]–H + $2H_2O$	Step 2 – Heyrovsky step (2-H) [PEDOT^0]–H + H_2O + H_3O^+ + e → [PEDOT^0] + H_2 + $2H_2O$
Step 3 – Tafel step (3-T) H–[PEDOT^0]–H + $2H_2O$ → [PEDOT^0] + H_2 + $2H_2O$	
Overall: [PEDOT^0] + $2H_3O^+$ + 2e → [PEDOT^0] + H_2 + $2H_2O$	

Scheme S1. Reactions steps of heterogeneous HER

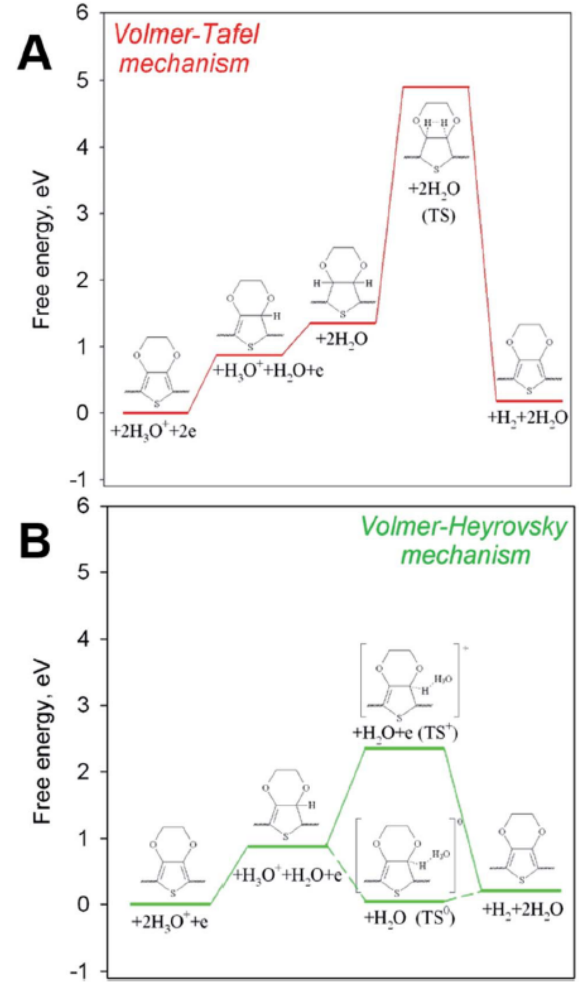
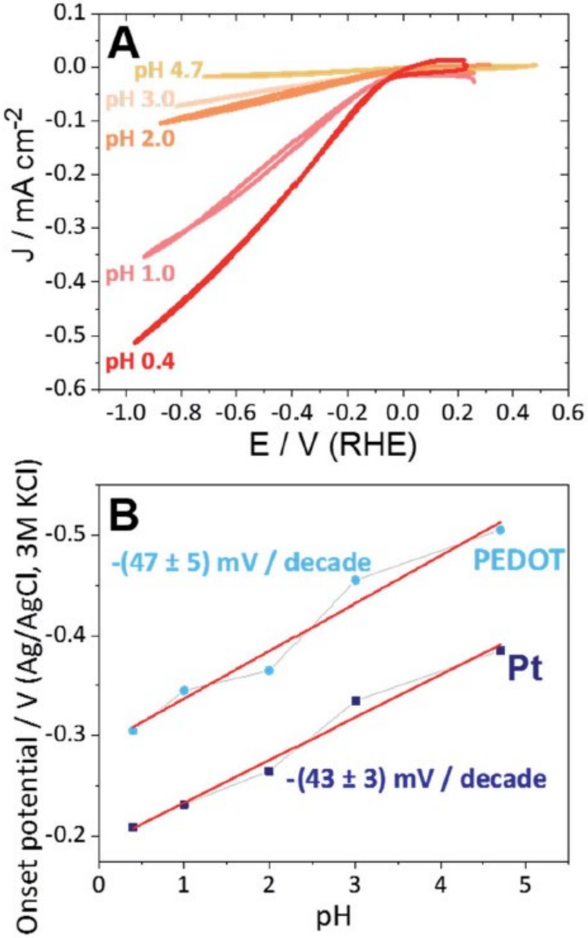
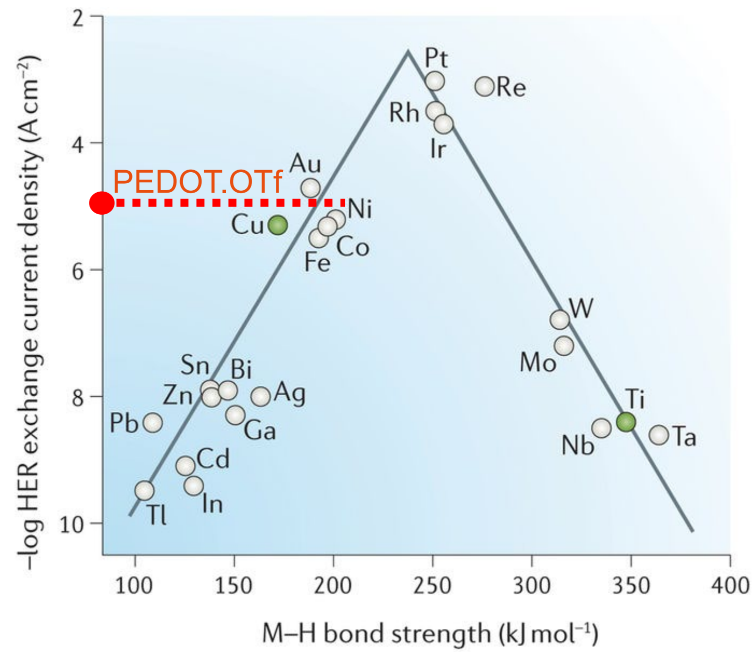


Fig. 4 Free energy diagrams for the HER on PEDOT–PEG: the Volmer–Tafel mechanism (red) and the Volmer–Heyrovsky mechanism (green).

• pH dependency



pH effect on the HER. (A) Cyclic voltammograms obtained for PEDOT–PEG electrodes in nitrogen-saturated 0.5 M H_2SO_4 solution with different pH values adjusted with NaOH; scan rate 5 mV/s; (B) pH dependences of the apparent HER onset potential for PEDOT–PEG and platinum.



PEDOT reaches an exchange current density comparable to that of metals (*i.e.* Cu, Ni, and Au) and in addition does not form passivating oxide layers or suffer from chemical corrosion in acidic media.

R.Valiollahi, et. al., Sustainable Energy Fuels 3 (2019) 3387–3398
I. Roger, et al., Nat. Chem. 1 (2017) 0003

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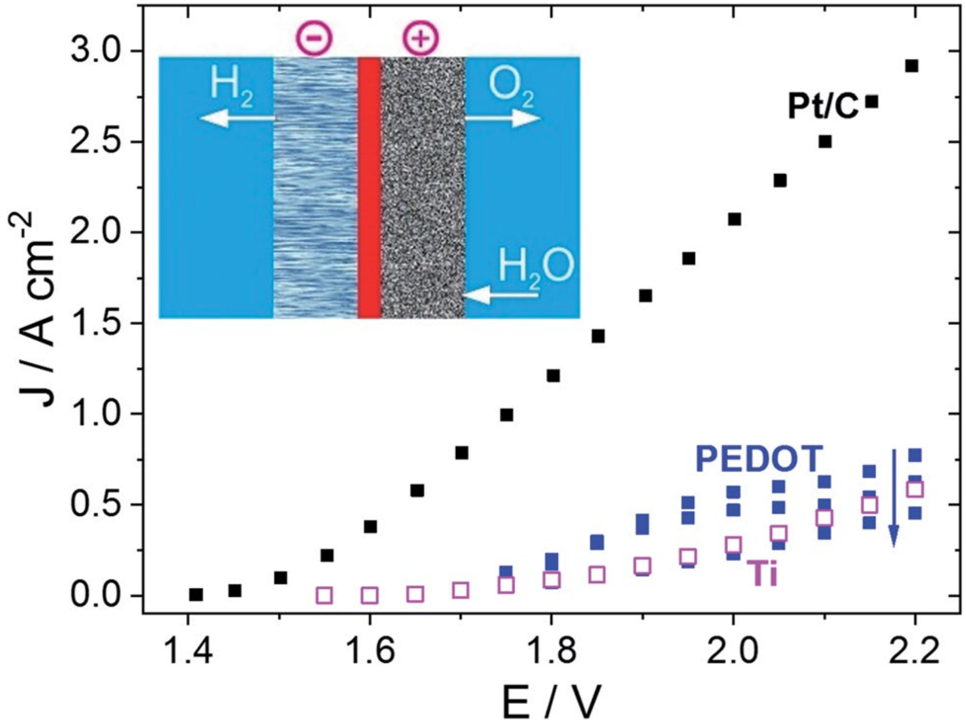
- **Performance of the PEDOT electrode in a Polymer Electrolyte Membrane Water Electrolyzer (PEMWE)**



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 the 1st to the 3rd day.

- The film was degrading during continuous cycling.
- The optimization for the thickness is needed.
- The results open new doors to metal-free polymer as electrocatalyst for the hydrogen production.

R.Valiollahi, et. al., Sustainable Energy Fuels 3 (2019) 3387–3398

- **Performance comparison a Polymer Electrolyte Membrane Water Electrolyzer (PEMWE)**

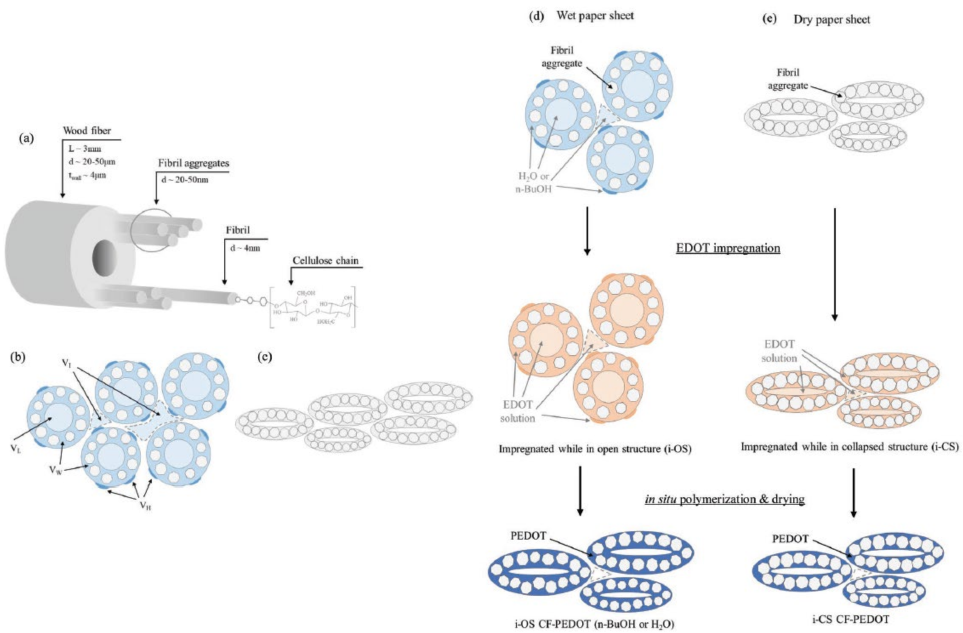
Table 3 Performance characteristics of different PEMWEs based on PGM-free cathodes

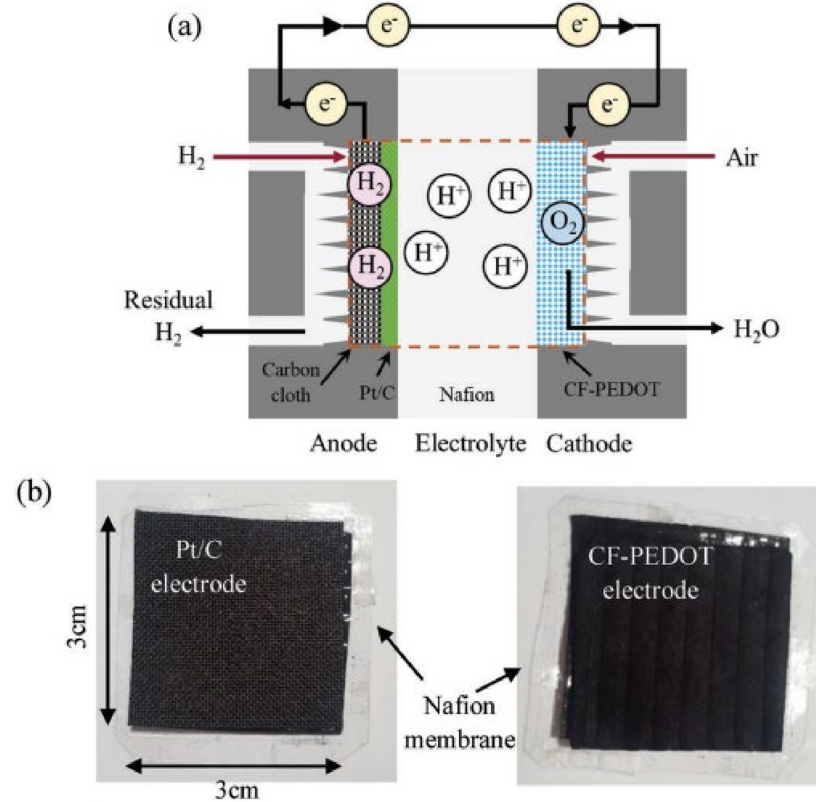
Cathode catalyst	Operational temperature, °C	Nafion thickness, μm	Overpotential at 0.5 A cm^{-2}, V	Reference
PEDOT	80	183	1.95	**Present work**
$Fe(Cl_2Gm)_3(BC_6H_5)_2$	80	183	1.95	49
$Fe((Phen(CH_2)_3S)_2Gm)_3(Bn\text{-}C_4H_9)_2$	80	183	1.99	68
MoS_2 on Vulcan	80	183	2.0	51
MoS_x on carbon black	80	127	1.85	47
Mo_3S_{17} on carbon black	80	127	1.8	47
FeS_2 on carbon	80	127	2.0	50
$Cu_{93.7}Mo_{6.3}$	90	50.8	1.9	48
MoS_x on carbon paper	90	50.8	1.95	46
$Ni_{0.64}Co_{0.36}O_xS_{0.14}$	90	50.8	1.97	45

*PGM-free: platinum group metal-free

45. H. Kim, et. al., Appl. Catal., B, 2018, 232, 93–100.
46. J. H. Kim, et al, J. Power Sources 392 (2018) 69–78.
47. C. Karlsson, et. al., Electrochim. Acta, 179 (2015) 336–342.
48. H. Kim, et al., Appl. Catal. B, 206 (2017) 608–616.
49. S. A. Grigoriev, et al., Int. J. Hydrogen Energy 42 (2017) 27845–27850.
50. C. Di Giovanni, et al., ACS Catal. 6 (2016) 2626–2631.
51. T. Corrales-Sanchez, et. al.,Int. J. Hydrogen Energy 39 (2014) 20837–20843.
68. O. A. Varzatskii, et al., Int. J. Hydrogen Energy 42 (2017) 27894–27909.

• PEDOT as a cathode electrode





➢ PEDOT is already studied as the electrode material for oxygen Reduction Reaction (ORR) for a disposable fuel cell.

➢ In principle an electrolyzer or Fuel cell can be run with two metal-free electrodes made of PEDOT.

Adv. Sustainable Syst. 3 (2019) 1900097-1900105.

Conclusion and Outlook

- PEDOT-PEG as a true all-organic polymer electrocatalyst system for the hydrogen evolution reaction (HER) with efficient electrical-to-chemical energy conversion and good stability in acidic media was fabricated.
- The organic electrode for H_2 production was used in an electrolyser.
- This might be extrapolated to other non-metallic organic electrocatalysts and that a molecular design of the catalytic activity can be further explored.
- The film optimum thickness and physical durability for long term application shall be studied.

Thank You

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