Supporting Information

Towards High-Temperature Fuel Cells using Sulfonated-Phosphonated Poly(pentafluorostyrene)

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Materials and Methods

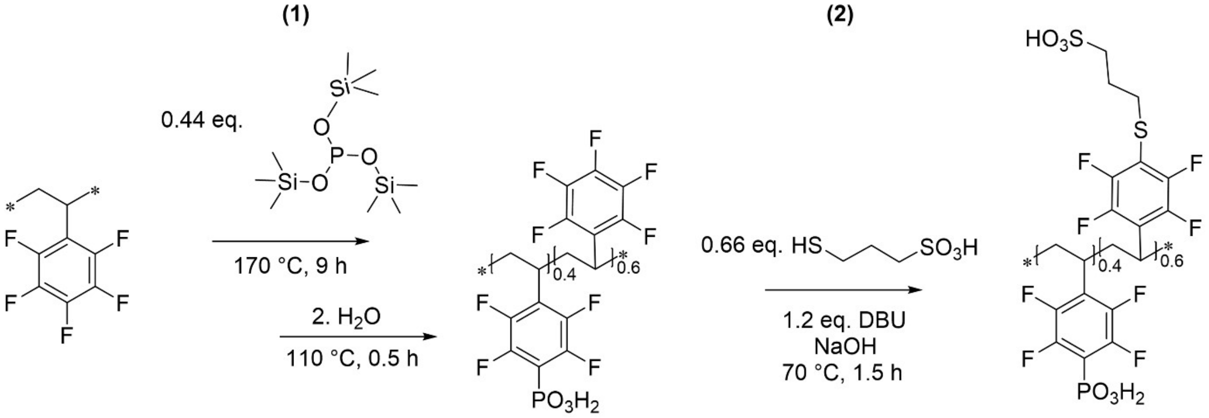
Manchester Organics was the supplier for tris(trimethylsilyl)phosphite (TSP). 3-Mercapto-1-propanesulfonic acid sodium salt (MPS) was purchased from Fluorochem and poly[2,2′-(*p*-oxydiphenylene)-5,5′-bibenzimidazole] (O-PBI) with a number/mass average molar mass of M_n/M_w = 20/24 kg mol^{-1} was obtained from Fumatech. Further chemicals and solvents were obtained from Sigma-Aldrich. The chemicals were used without further purification. The Nafion membrane (N-211) from Fuel Cell Store was used as a reference without further posttreatment. Poly(pentafluorostyrene) was synthesized as described in previous literature.[1] As a phosphonated reference material PWN75 (1) was chosen and synthesized as specified in the work of Atanasov and Kerres.[2]

Synthesis of PWN40-S

PPFS (8 g, 0,0413 mol) was dissolved in DMAc (20 mL) in a round-bottom flask equipped with a reflux condenser under inert atmosphere and TSP (0.44 eq., 5.77 mL, 0.0182 mol) was added. The reaction mixture was vigorously stirred for nine hours at 170°C. Afterward, deionized water was added to the solution. The white swollen solid was heated to 110°C and hydrolyzed for 30 min. Herein, the water was changed three times. The solid was conditioned in 10 wt% H_2SO_4 at 70°C for 4 h and washed with water till the pH was neutral. After drying at 85°C a white solid was obtained. By the integral ratio between the resonances corresponding to the substituted (-135 ppm) and the non-substituted (-163 ppm) pentafluorophenyl rings of PPFS in the ^{19}F NMR the phosphonation degree was determined. ^{1}H NMR (500 MHz, DMSO-d6, δ [ppm]): 7.90; 2.83; 2.31; 1.91. ^{19}F NMR (470 MHz, DMSO-d6, δ [ppm]): -134; -142: -157; -163. ^{31}P NMR (202 MHz, DMSO-d6, δ [ppm]): -0.95.

Sulfonic acid groups are introduced via the Para-fluoro-thiol reaction with 3-mercapto-1-propanesulfonic acid sodium salt. PWN40 (5.32 g, 0.0243 mol) is mixed with NaOH (0.1 M, 50 mL) 3-mercapto-1-propanesulfonic acid sodium salt (0.66 eq., 2.86 g, 0.0160 mol), and 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) (1.2 eq., 7.25 mL, 0.3124 mol + 0.0194 acid mol). After stirring the reaction mixture for 1.5 h at 70°C the yellowish reaction solution was precipitated in 2-propanol, filtered, and washed with 2-propanol (200 mL). To convert the product into H^+ form the solid was stirred in 10 wt% H_2SO_4 at 70°C for 4 h. Afterward, the acidic solution was dialyzed (dialyzing tubes MWCO 6000-8000 g mol^{-1}) for three days, exchanging the water three times per day. Drying the solid at 85°C afforded a white-yellowish powder with a yield of 71%. ^{1}H NMR (500 MHz, DMSO-d6, δ [ppm]): 3.42; 3.21, 2.88; 2.52; 1.88; 1.51. ^{19}F NMR (470 MHz, DMSO-d6, δ [ppm]): -135; -145. ^{31}P NMR (202 MHz, DMSO-d6, δ [ppm]): -0.3.

[1] Note: PWN75 refers to a phosphonation degree of 75%, while PWN40 has a degree of phosphonation of 40% in the following study.



Scheme S1. Synthesis of PWN40-S: (1) S_NAr Michaelis-Arbuzov Reaction, (2) Para-fluoro-thiol reaction.

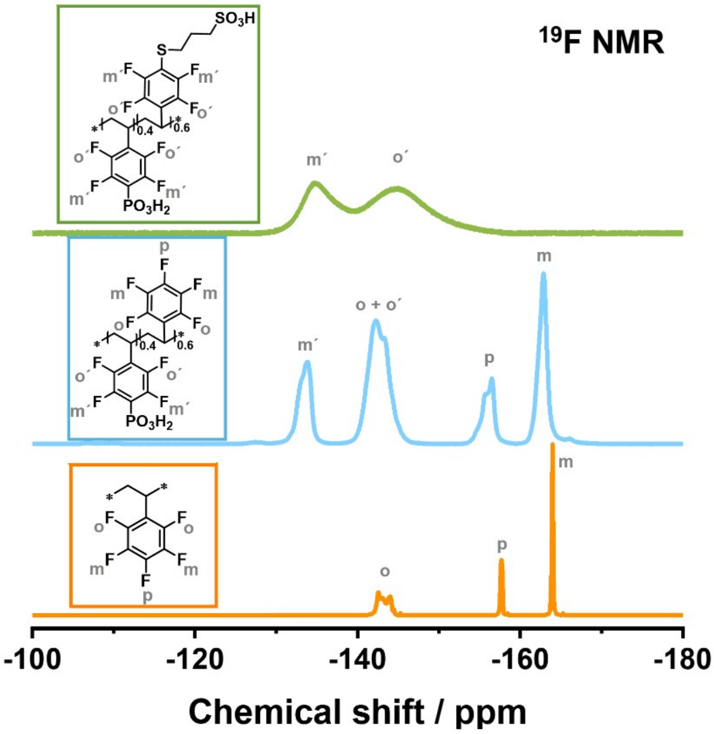


Figure S1. ^{19}F NMR of (orange) PPFS (solvent: Acetone-d_6), (blue) PWN40 (solvent: DMSO-d_6), and (green) PWN40-S (solvent: DMSO-d_6).

Fourier transform infrared spectroscopy

A 3 FT-IR spectrometer from PerkinElmer was utilized to measure FT-IR spectra from polymer samples of PPFS, PWN40, and PWN40-S. An ATR unit and a wavenumber range from 4000 cm^{-1} to 650 cm^{-1} were employed. The signals were assigned using the references[2,3].

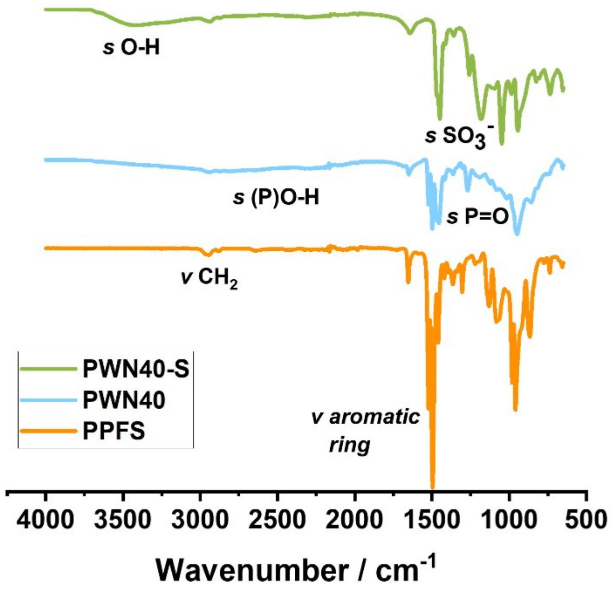


Figure S2. FT-IR spectra of PPFS, PWN40, and PWN40-S.

Thermal Stability

The stability against heat of the synthesized polymers was investigated by thermogravimetric analysis (TGA800, PerkinElmer). A heating rate of 10°C min^{-1}, a gas flow rate of 30 mL min^{-1}, and synthetic air as gas environment were chosen.

Differential Scanning Calorimetry

Richardson's method [4] was applied to determine the glass transition temperatures. A differential scanning calorimetry (DSC 3+, Mettler Toledo) with a heating rate of 10 K min^{-1} under a nitrogen atmosphere and a flow rate of 50 mL min^{-1} was used.

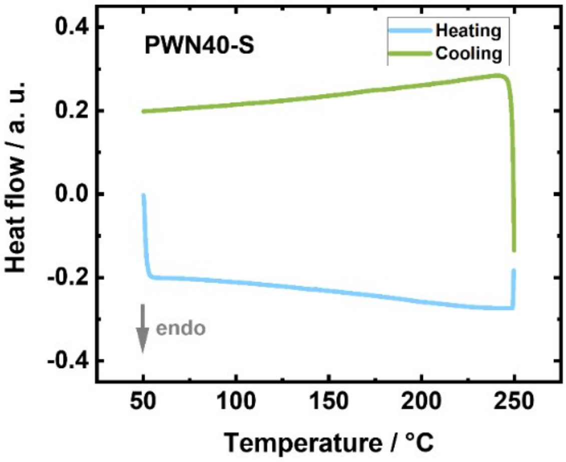


Figure S3. DSC analyses of PWN40-S (heating rate = 10 K min^{-1}, nitrogen atmosphere flow rate = 50 mL min^{-1}).

Membrane preparation

PWN40-S and PWN75 were dissolved in dimethyl sulfoxide (DMSO) (5 wt%) and neutralized with triethanolamine at 60°C for 24 h. A poly[2,2'-(*p*-oxydiphenylene)-5,5'-bibenzimidazole] (O-PBI) solution (5 wt% in DMSO) was added to obtain an overall IEC of around 3.0 meq. g^{-1}. Herein, die PWN40-S blend membrane has an O-PBI content of 18 wt%, whereas the PWN75 blend membrane a content of 32 wt%. After homogenization, the solutions were cast with a doctor blade on a glass substrate. The solvents were evaporated at 80°C over night. After detaching the membranes from the glass substrate in a water bath, the membranes were conditioned in a 10 wt% H_2SO_4 solution for 48 h at 85°C. Then, the films were washed in water at 85°C for 48h frequently exchanging the water.

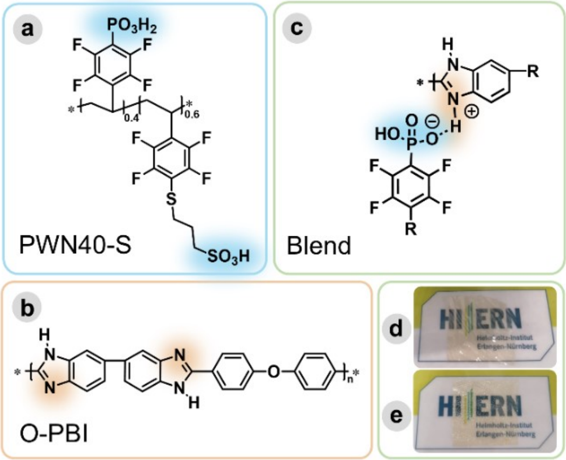


Figure S4. Chemical structure of (a) PWN40-S and (b) O-PBI. (c) Ionically crosslinking between the phosphonic moiety and the amine group of the benzimidazole. (d) Picture of blend membrane PWN40-S + O-PBI (18 wt%) and (e) of PWN75 + O-PBI (32 wt%).

N_2 - sorption

The surface area of the synthesized polymer PWN40-S and the membranes, PWN40-S + O-PBI, PWN75 + O-PBI, and the reference membrane N211 was determined via nitrogen physisorption at liquid nitrogen temperature using a Quadrasorb SI analyzer (Quantachrome Instruments) and analyzed with the Brunauer-Emmett-Teller (BET) method. The samples were degassed for 24 h at 150°C with a pressure of 0.01 mbar prior to all measurements.

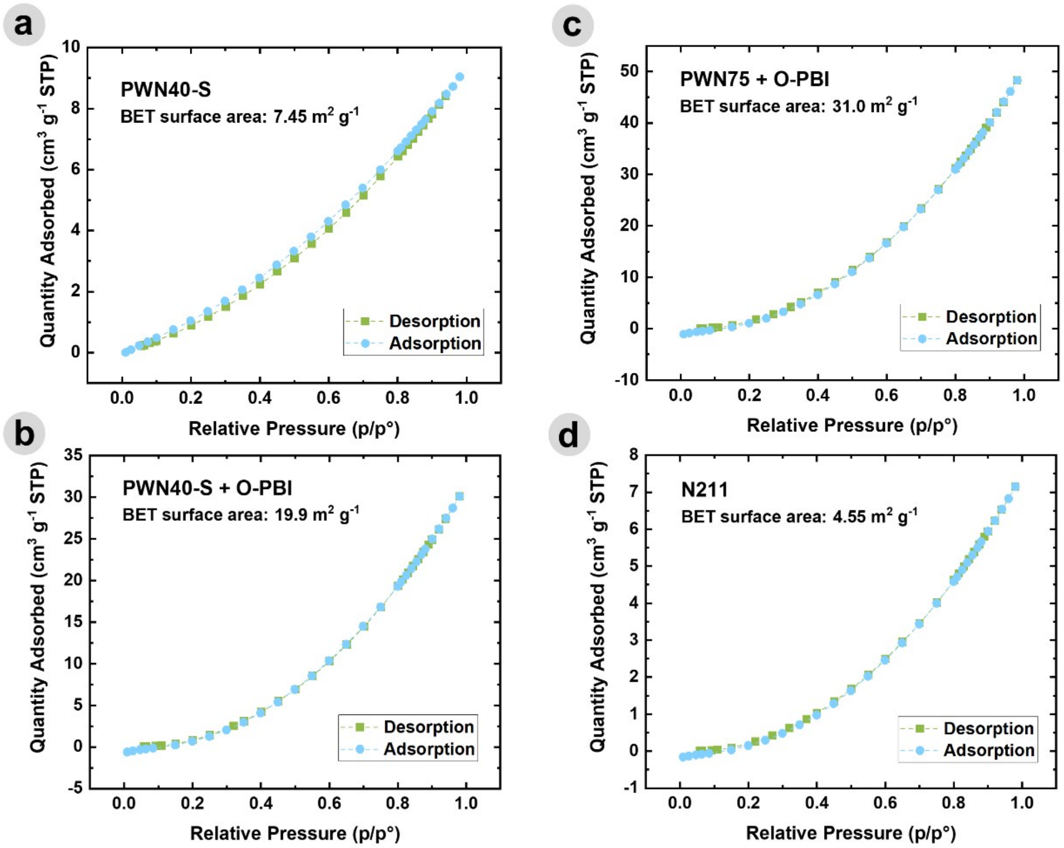


Figure S5. N_2 adsorption/ desorption isotherms at 77 K for BET surface area analysis of (a) the polymer PWN40-S, (b) the blend membrane PWN40-S + O-PBI, (c) the blend membrane PWN75 + O-PBI, and (d) the reference membrane N211.

Tensile testing.

Mechanical properties of the fabricated membranes were derived via a tensile tester (EZ-SX, SHIMADZU Corporation, Japan) at atmospheric environment (T = 22.6 ± 0.1°C, RH = 23 ± 1.0%). The Young's modulus, tensile strengths, and the elongation of breaks of the membranes with a thickness of 30 µm and an area of 1 cm x 4 cm were determined at an extension rate of 5 mm min^{-1}. In the interest of reproducibility at least four membrane pieces of each membrane type were tested.

Table S1. Tensile tests of fabricated blend membranes at T = 22.6 ± 0.1°C, RH = 23 ± 1.0%.

	PWN40-S + O-PBI	**PWN75 + O-PBI**	**O-PBI**
Young's Modulus / GPa	1.01 ± 0.5	0.60 ± 0.2	1.46 ± 0.6
Tensile Strength / MPa	44.5 ± 9.5	50.4 ± 4.1	58.6 ± 18.1
Elongation at Break / %	11.5 ± 3.7	8.46 ± 1.2	7.08 ± 3.3

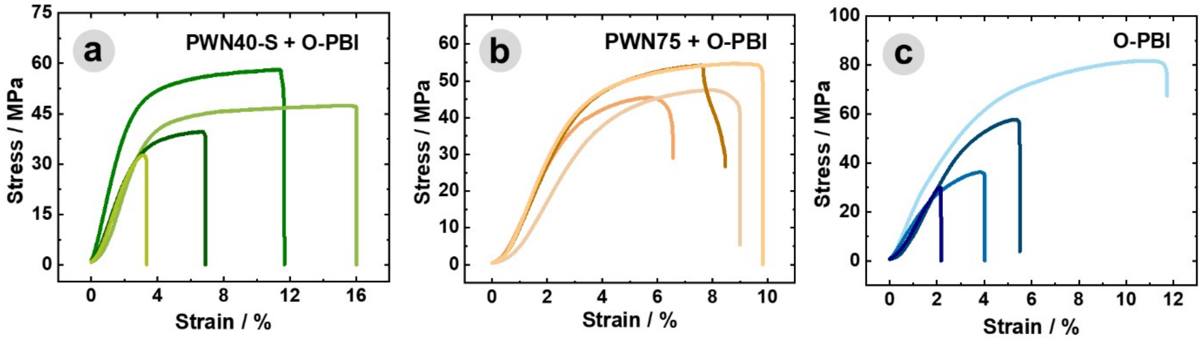


Figure S6. Stress-strain profiles of the fabricated membranes consisting of (a) PWN40-S + O-PBI, (b) PWN75 + O-PBI, and (c) O-PBI.

High-angle annular dark-field scanning transmission electron microscopy (HAADF STEM)

An aqueous concentrated Barium acetate solution was used to stain a 1 cm^2 piece of PWN40-S blend membrane for 5 h at 60°C. Residual Ba^{2+}-ions were removed by washing the membrane several times in deionized water. The treated sample was then embedded in epoxy resin (Araldite 502) and subsequently sliced using an RMC Boeckeler PowerTome equipped with a Diatome 45° diamond knife, with deionized water in the knife boat. The nominal section thickness was set to 75 nm, and the section was placed on a lacey carbon-coated Cu TEM grid. Structural and compositional characterization was performed using a ThermoFisher Scientific Talos F200i (S)TEM. HAADF-STEM was employed to achieve mass-thickness contrast, with an acceleration voltage of 200 kV. Further spectrum imaging was carried out using a Dual Bruker XFlash 6 | 100 EDS detector.

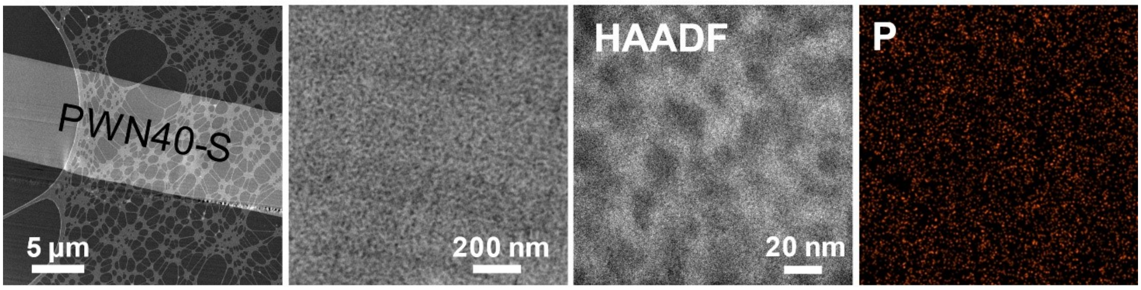


Figure S7. HAADF-STEM images of the PWN40-S blend membrane with corresponding phosphorous EDX spectrum.

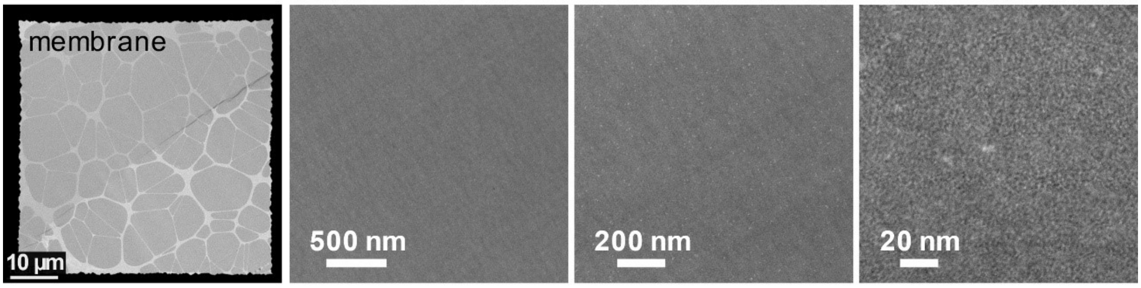


Figure S8. HAADF-STEM images of the PWN75 blend membrane.

Ion exchange capacity

Ion exchange capacities (IEC_{direct} and IEC_{total}) of the membranes were obtained by salt splitting titration method at room temperature using an OMNIS-titrator of Metrohm. The membranes were immersed in saturated sodium chloride solution for 24 h at 85°C. The exchanged H^+ ions were then titrated with 0.1 M NaOH to the equivalent point (IEC_{direct}) and a defined excess of NaOH was added. This solution was back titrated with 0.1 M HCl, and the IEC_{total} was calculated. IEC values are determined from the titration results using the formula: IEC_{direct} [(mequiv.)⁄g] = $(V_{EP,NaOH} \times M_{NaOH})/W_{membrane}$; IEC_{total} [(mequiv.)⁄g] = $[(V_{NaOH} \times M_{NaOH} - V_{EP,HCl} \times M_{HCl})/W_{membrane}] + IEC_{direct}$, where $V_{EP,\ NaOH}$ is the volume in mL of NaOH at the equivalent point, V_{NaOH} is the total volume of added NaOH, M_{NaOH} the molecular weight of NaOH, $V_{EP,\ HCl}$ the volume of HCl at the equivalent point, M_{HCl} the molecular weight of HCl and $W_{membrane}$ the weight of the dried membrane in the acidic form. The titration was performed three times for each sample, taking the average value for $IEC_{dircect}$ and IEC_{total}.

Impedance measurements.

Electrochemical impedance spectroscopy over the frequency range of 1 KHz – 10 MHz was applied to obtain through-plane conductivities at room temperature. An AC impedance technique was used with an electrochemical workstation Zennium X of Zahner equipped with a separate conductivity cell. 0.5 M H_2SO_4 was used as an electrolyte. The proton conductivities of the membranes were calculated by $\sigma = L/(R \times A)$, where σ is defined as the reciprocal of R with the unit Siemens per centimeter [S cm^{-1}]. R is the resistance [Ohm], L the membrane thickness [cm], and A the area of the gold electrodes [0.25 cm^2]. The measurement of each membrane was performed five times, taking the average value for the proton conductivity.

Furthermore, temperature-dependent through-plane conductivities were performed using a membrane testing setup (Scribner Associates Inc., MTS 740) coupled with an impedance analyzer (Newton 4th ltd, NumetriQ, Model: PSM 1735). An AC frequency range of 10 MHz to 100 Hz with an AC amplitude of 10 mV was applied. Gas diffusion layers (Freudenberg H23C2, Fuel Cell Store) were attached with conductive carbon paint (Electrodag 502, Fluoroelastomer binder, Plano GmbH) to the platinum electrodes of the testing rig. The membrane electrode assembly was compressed with around 1.4 psi and the back pressure was set to 1.9 bar for all measurements. The membrane impedances were obtained by fitting the Nyquist plots with an open circuit model (Figure S5). The displayed mean error in the measurements is dependent on the fluctuation of relative humidity and inductive effects. The proton conductivities of the membranes were obtained from $\sigma = L/(R \times A)$, where R is the resistance [Ohm], L the membrane thickness [cm], and A the overlapping area of the electrodes [0.5 cm^2]. Herein, a temperature-dependent conductivity measurement of the reference membrane PWN75 + O-PBI could not be analyzed due to diminished conductivity.

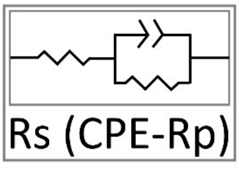


Figure S9. Circuit model used to fit impedance data.

Activation energy (Ea).

The activation energy, which is an indication of how easily proton conduction occurs, was determined using the Arrhenius equation: $\ln \sigma = \ln \sigma_0 - Ea / (RxT)$, where σ is the proton conductivity and σ_0 the pre-exponential factor [mS cm^{-1}], Ea is the activation energy [kJ mol^{-1}], R is the gas constant [J mol^{-1} K^{-1}], and T is the temperature [K].

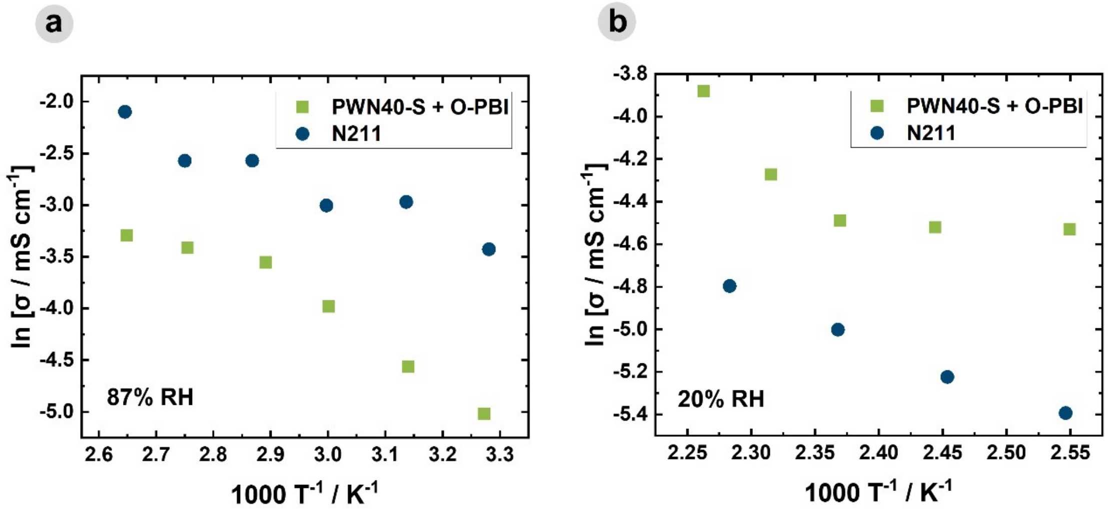


Figure S10. Arrhenius plots of proton conductivities (a) under 87% RH, 30-100°C and (b) under 20% RH, 120°-170°C.

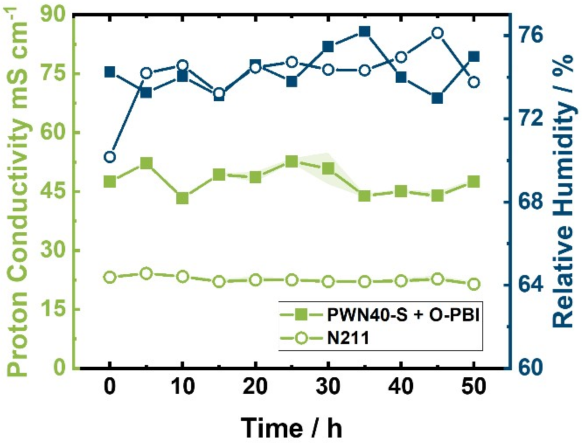


Figure S11. Long-time proton conductivity measurement of the PWN40-S blend membrane and the reference membrane N211 at 120°C, with the respective relative humidity.

Water uptake (WU).

The membranes were weighed in their dry state (W_{dry}). Subsequently, the membranes 'wet' weights (W_{wet}) are measured after equilibrating in water for one day at 85°C. The total water content was calculated from the difference between the wet and the dry mass of the membranes: Water Uptake [%] = $[(W_{wet} - W_{dry})/W_{dry}] \times 100$. Three membranes were measured for each polymer type, taking the average for the water uptake.

Volume swelling.

The volume swelling was obtained via a 3-fold determination calculating the difference between the wet and the dry volume change of the membranes after one day at 85°C: Volume Swelling [%] = $[((W\times L)_{wet} - (W\times L)_{dry})/(W\times L)_{dry}] \times 100$, where W is the width, and L is the length of the membrane.

Stability against acidic medium.

The stability against an acidic environment was investigated in a 10 wt % H_2SO_4 solution for 21 days. The H_2SO_4 solution was afterward analyzed via NMR, specifically collecting ^{31}P NMR and ^{19}F NMR spectra, to examine degradation moieties of the polymer structure. The membrane pieces with an area of 4 cm^2 were washed with deionized water, dried at 85°C and weighed. The mass loss was calculated from the difference between the dry weight before and after the acid stability test: Mass loss [%] = $[(W_{after} - W_{before})/W_{after}] \times 100$.

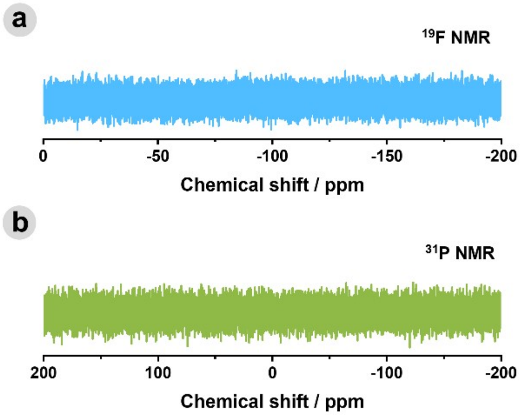


Figure S12. (a) ^{19}F NMR and (b) ^{31}P NMR of H_2SO_4 solution after 21 days.

Fenton´s test.

To investigate the chemical stability of PWN40-S+O-PBI and N211 membrane a Fenton´s test was carried out. Herein, oxygen radical species were formed with an aqueous solution of 3 wt% H_2O_2 and 4 ppm Fe^{2+} ions ($FeSO_4$ ▪$7H_2O$). The membranes were immersed in the Fenton´s solution for 2h and 6h at 80°C. Afterward, the membranes were washed with water, dried, and weighed. The mass loss was calculated from the difference between the dry weight before and after: Mass loss [%] = $[(W_{after}\ W_{before})/W_{after}] \times 100$. To investigate degraded components, ^{19}F NMR were collected from the Fenton´s solution. Furthermore, ^{19}F NMR and ^{1}H NMR of the membrane pieces were collected before and after the Fenton´s test.

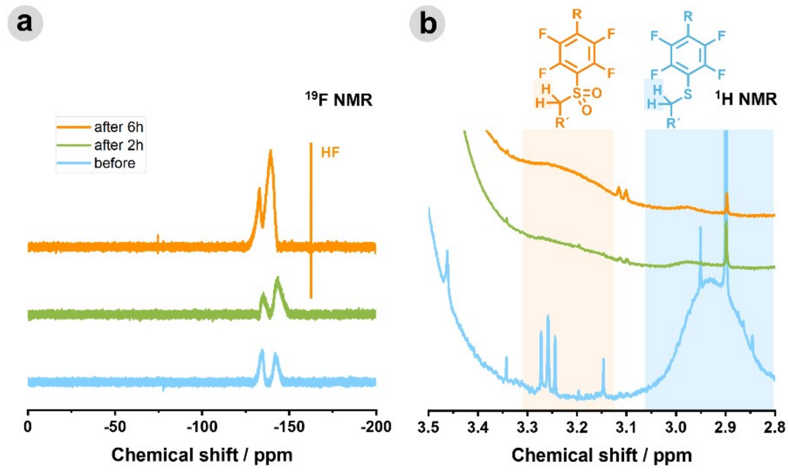


Figure S13. (a) ^{19}F NMR (b) ^{1}H NMR of PWN40-S + O-PBI membrane before and after the Fenton´s test (solvent: d$_6$-DMSO), (c) ^{19}F NMR of Fenton´s solution after 2h and 6h.

Table S2. Comparison of membrane properties of PWN40-S + O-PBI, PWN75 + O-PBI, with the reference membrane N211. (*) measured at RT with Zennium X of Zahner with 0.5 M H_2SO_4 electrolyte. (**) measured with MTS setup equipped with temperature and humidity control.

	PWN40-S + O-PBI	**PWN75 + O-PBI**	**N211**
BET surface area / m^2 g^{-1}	19.9	-	4.55
Mass loss, 10wt% H_2SO_4 after 504h at 85°C / %	6.1 ± 0.4	4.7 ± 0.7	-
Mass loss, Fenton´s test after 2h at 80°C/ %	0.11 ± 0.06	-	0.9 ± 0.54
Mass loss, Fenton´s test after 6h at 80°C/ %	1.1 ± 0.8	-	1.6 ± 0.5
Proton conductivity (*) at RT / mS cm^{-1}	40.0 ± 1.8	-	55.9 ± 0.4
Proton conductivity (*) at RT after 2h Fenton´s test / mS cm^{-1}	39.2 ± 1.6	-	45.6 ± 0.2
Proton conductivity (*) at RT after 6h Fenton´s test / mS cm^{-1}	35.9 ± 1.2	-	43.9 ± 0.5

Proton conductivity (**) at 120°C, 87% RH / mS cm^{-1}	76.3 ± 9.3	-	54.0 ± 11.5
Proton conductivity (**) at 170°C, 20% RH / mS cm^{-1}	20.6 ± 3.3	-	8.3 ± 1.7
Ea 30-100°C, 87% RH / kJ mol^{-1}	32.7 ± 0.9 (30-75°C) 9.0 ± 0.5 (75-100°C)	-	14.4 ± 0.8
Ea 120-170°C, 20% RH / kJ mol^{-1}	5.4 ± 1.9 (120-150°C) 40.3 ± 7.0 (150-170°C)	-	19.4 ± 1.1

References

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