<div align="center">Supporting Information</div>

Tetrazole functionalization: A new strategy toward stable alkaline ion-solvating polymer electrolytes

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S1 Experimental

S1.1 Materials

Poly(styrene-*co*-acrylonitrile) (SAN$_{25}$: 25 wt% acrylonitrile, M_w = 165,000 g mol^{-1}, Sigma-Aldrich; SAN$_{30}$: 30 wt% acrylonitrile, M_w = 185,000 g mol^{-1}, Sigma-Aldrich), NH$_4$Cl (99.5%, Sigma-Aldrich), NaN$_3$ (99.5%, Sigma-Aldrich), K$_2$CO$_3$ (99%, Sigma-Aldrich), CH$_3$I (99.0%, Sigma-Aldrich), 5-phenyl tetrazole (99%, Sigma-Aldrich), N(CH$_3$)$_4$Cl (98%, TCI Europe N.V.), *N,N*-dimethylformamide (DMF, 99.8%, anhydrous, Sigma-Aldrich), methanol (MeOH, 99.8%, Sigma-Aldrich), tetrahydrofuran (THF, >99.9%, Sigma-Aldrich), aqueous HCl (37%, Sigma-Aldrich) and KOH pellets (90%, Sigma-Aldrich) were used as received. The aqueous KOH solutions were prepared by dissolving the KOH in MilliQ water, and the concentration was determined by comparing the density with literature data. Nickel foam (mean cell size 450 μm, thickness 1600 μm) was obtained from Alantum. Zirfon Perl UTP 500 (50 ± 10 % porosity) was supplied by Agfa.

S1.2 Stability assessment and computational methods

15 mL of a 25 wt% aqueous KOH solution containing 5-phenyl tetrazole (50 mL) and $N(CH_3)_4Cl$ (25 mM, as internal standard) was prepared by dissolving in MilliQ water in a 50 mL poly(tetrafluoroethylene) (PTFE) test tube. A 0.5 mL sample was taken out for ^1H NMR analysis, and the tube was then sealed and kept at 80 °C for nearly 4000 h. Sampling was carried out regularly by taking out 0.5 mL of the liquid from the tubes after it had been cooled to room temperature. The concentration of 5-phenyl tetrazole was calculated from the sample to internal standard peak integral ratio, assuming that the $N(CH_3)_4Cl$ concentration remained constant.

S1.3 Computational methods

The 6-311++G(d,p) basis sets and B3LYP functional, as implemented in Q-Chem 6.0, were used for all optimized geometries and calculated energies. 3.0×10^{-3} Hartree/Bohr and 1×10^{-8} Hartree, respectively, were the thresholds for the maximum gradient and the self-consistent field (SCF) energy shift between successive optimization cycles. Using the optimized gas-phase geometries as a basis, the conductor-like polarization continuum model (C-PCM) was used to determine single point energies. To incorporate the effect of the surrounding water medium, a relative dielectric constant of 78.39 with respect to the bulk water was chosen. The pK_a value was computed under identical experimental circumstances with T = 80 °C and 1 atm.

S1.4 Synthesis and film formation

Tetrazolation of SAN$_{25}$ and SAN$_{30}$: To a solution of SAN$_{25}$ (1.00 g, 5.7 mmol acrylonitrile units) in DMF with a concentration of 5 wt%, NaN_3 (1.50 g, 23.1 mmol) and NH_4Cl (1.24 g, 23.1 mmol)

were added. The reaction mixture was then stirred at a temperature of 130 °C for 48 h. The crude solution was thereafter poured into 1 M aqueous HCl to precipitate the polymer, which was isolated by filtration, and then redissolved in THF. The solution was again poured into a 1 M aqueous HCl and the precipitated polymer STz_{25} was filtered, washed extensively with deionized water, dried in a vacuum oven at 50 °C overnight and obtained in 98% yield. Using the same procedure, STz_{30} was synthesized from SAN_{30} (1.00 g, 5.5 mmol acrylonitrile units), NaN_3 (1.45 g, 22.4 mmol) and NH_4Cl (1.20 g, 22.4 mmol). After work-up and drying, STz_{30} was obtained in 97% yield.

Methylation of STz25 and STz30: STz_{25} (1.00 g, 2.2 mmol Tz units) was dissolved in DMF, followed by addition of K_2CO_3 (0.62 g, 4.4 mmol) and CH_3I (0.56 mL, 8.8 mmol). The mixture was stirred overnight at room temperature and thereafter poured into deionized water to precipitate the polymer, which was isolated by filtration. The precipitate was then redissolved in THF and precipitated again. The resulting yellow solid was filtered, washed with deionized water, and dried in a vacuum oven at 50 °C overnight, resulting in a yield of 99%. Similarly, STz_{30} (1.00 g, 2.7 mmol tetrazole units) was methylated using the same procedure with K_2CO_3 (0.74 g, 5.4 mmol) and CH_3I (0.67 mL, 10.7 mmol) and obtained in 99% yield.

Membrane casting: To prepare the membranes, homogeneous solutions of STz_{25} and STz_{30} in DMF with a solid content of 10% were prepared. These solutions were then poured onto Petri dishes placed on a horizontal glass plate, and the solvent was evaporated at 80 °C with filter paper covering the dishes. After the solvent evaporation, the resulting membranes were carefully delaminated from the glass substrates by immersing in deionized water. The membranes were stored in water until used.

S1.5 Characterization

The ^{1}H NMR spectra were acquired using a Magritek Spinsolve 80 spectrometer operating at 80 MHz. Deuterated dimethyl sulfoxide (DMSO-d_6) and chloroform (CDCl$_3$) were used as solvents. For the stability test of 5-phenyl tetrazole, the spectra were recorded with solvent suppression using the sampled material dissolved in KOH/H$_2$O without further workup. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded from 550 cm^{-1} to 4000 cm^{-1} using a PerkinElmer Spectrum Two FT-IR Spectrometer. Thermogravimetric analysis (TGA) was conducted using a Netzsch STA 449 F3 Jupiter instrument under an argon atmosphere from 25 to 700 °C at a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) was conducted using a Netzsch 200 F3 instrument under nitrogen atmosphere. The temperature range of 30-190 °C was employed for the pristine polymers, while the functionalized polymers were analyzed in the range of 30-140 °C. The samples underwent a heating-cooling-heating cycle with a heating rate of 10 °C min^{-1}. The glass transition temperature (T_g) was determined at the midpoint of the specific heat increment. X-ray diffraction (XRD) patterns of the polymers were obtained with a powder diffractometer (Panalytical, Aeris) at room temperature, with a scanning range for 2θ values of 5° to 55°. The membrane cross sections were examined using scanning electron microscopy (SEM) with a Zeiss EVO MA10 instrument. The samples were prepared by cryogenic fracturing in liquid nitrogen and subsequently sputter-coated with gold.

To determine the electrolyte uptake and swelling, circular samples with a diameter of 1 cm were dried in a vacuum oven at 60 °C overnight. The weight of the dried samples (W_{dry}) was measured. Subsequently, the samples were immersed in vials containing solutions of aqueous KOH with concentrations ranging from 5 to 25 wt% for 24 h. Afterward, the samples were carefully blotted with a lint-free cloth to remove excess liquid and weighed again to obtain the

electrolyte-imbibed membrane weight (W_{wet}). The electrolyte uptake (EU) was calculated using Equation 2.

$$EU = (W_{wet} - W_{dry}) / W_{dry} \qquad (1)$$

Similarly, the in-plane swelling ratio, SR, was calculated using Equation 2, where d_{dry} represents the diameter of the dry sample and d_{wet} represents the diameter of the electrolyte-imbibed sample.

$$SR = (d_{wet} - d_{dry}) / d_{dry} \qquad (2)$$

The ion conductivity measurements were performed using a two-compartment cell, where a membrane sample was placed between two Nickel perforated plate electrodes. The membrane samples were pre-soaked in KOH solutions with concentrations ranging from 5 to 25 wt%. The through-plane resistance of the membrane was determined at room temperature using electrochemical impedance spectroscopy (EIS) with a Gamry Reference 3000 instrument. The resistance R was taken as Z_{re} at $Z_{im} = 0$ Ω, and the conductivity (σ) was calculated as shown in Equation 3, where t and A is the thickness and surface area of the membrane, respectively.

$$\sigma = t / (R \times A) \qquad (3)$$

S1.6 Electrolysis testing

A single cell alkaline water electrolysis test was conducted using a 10 cm^2 flow cell. The membrane samples, pre-doped in a 15 wt% KOH solution for at least 24 h, were placed between

two Ni-foam electrodes that were densified by pressing to reduce their thickness from 1600 μm to 250 μm. The cell was sealed using flat sheet PTFE gaskets of suitable thickness. Heating and temperature monitoring were carried out directly within the end plates of the cell during the experiment. Gear pumps were used to circulate the electrolyte, and a 15 wt% KOH solution (300 mL) was pumped through the electrode compartments at a flow rate of 80 mL min^{-1}. The experiments were performed at atmospheric pressure and at a temperature of 60 °C.

Polarization curves were recorded stepwise with a duration of 60 s at each current density setpoint. Prior to recording the polarization curves, the system was activated for 24 h at a constant current density of 100 mA cm^{-2}. EIS was performed using a VersaStat 4 potentiostat in potentiostatic mode at a potential of 1.3 V. The frequency range for EIS measurements was from 100 kHz to 1 Hz with an amplitude of 10 mV. The cell operated at a constant current density of 100 mA cm^{-2} during the intervals between the polarization experiments and EIS measurements.

The H_2 crossover was measured sequentially at current densities of 50, 100, 150, 200, 300, 400, and 500 mA cm^{-2}. At each current density, the setpoint was maintained for 3400 s, and the hydrogen content on the anode side was measured using an electrochemical hydrogen sensor (Geopal Systems, GJ-EX with a H2/M-40000 detector) after passing through a silica gel column. To ensure consistent signal quality, a continuous nitrogen flow of 57 mL min^{-1} was applied to the system. The hydrogen permeability was calculated using methods described elsewhere.[1]
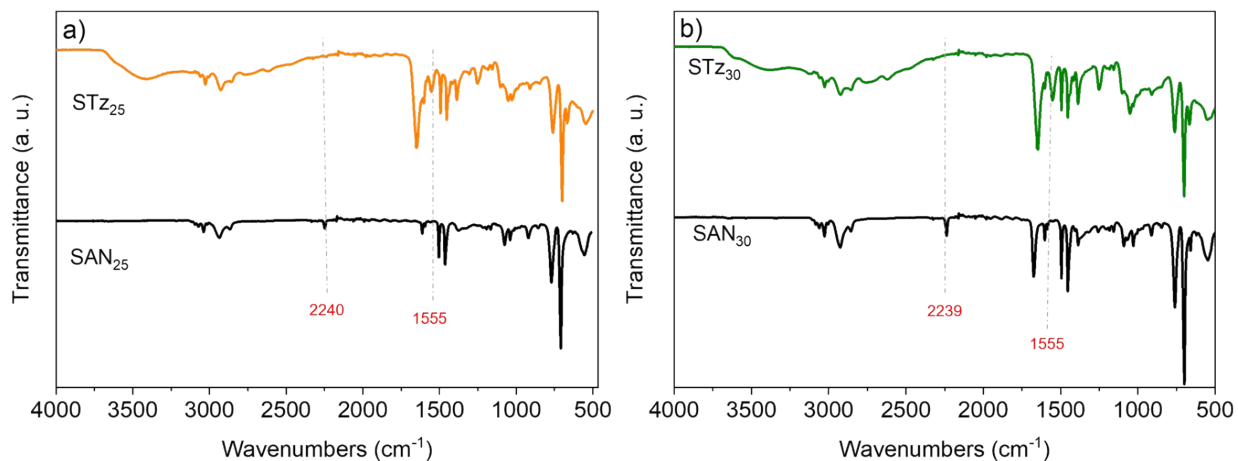
S2 Supplementary figures and tables

Figure S1 FTIR of STz_{25} (a) and STz_{30} (b) and the corresponding pristine polymers. The absorption bands around 1555 cm^{-1} and are characteristic for the tetrazole groups.[2]
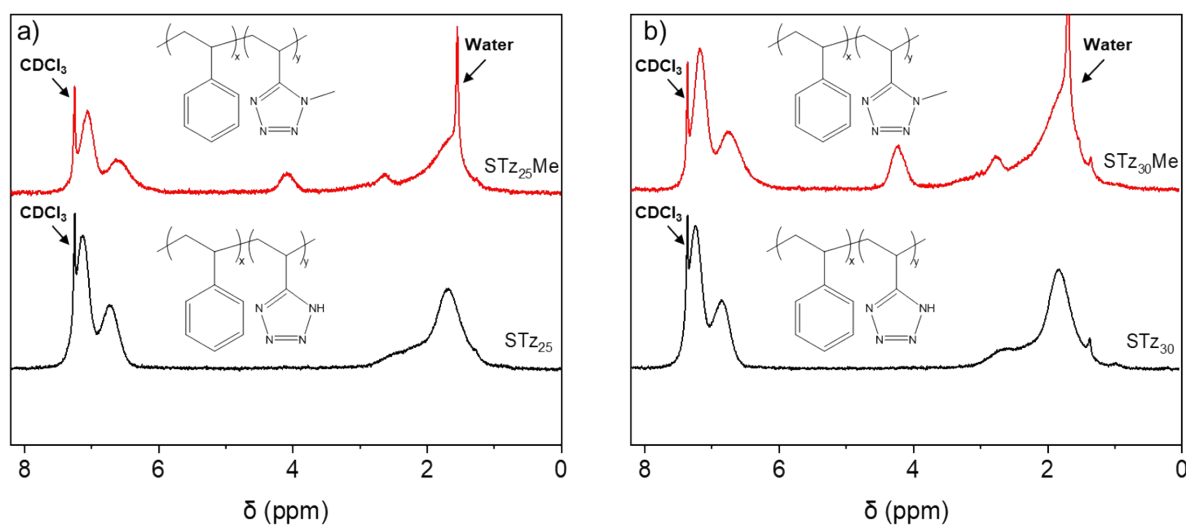

Figure S2 ^{1}H NMR of STz_{25} (a) and STz_{30} (b). Note that the tetrazole units were fully methylated (as described in literature[3]) to provide NMR trackable protons that could be used to determine the degree of functionalization.
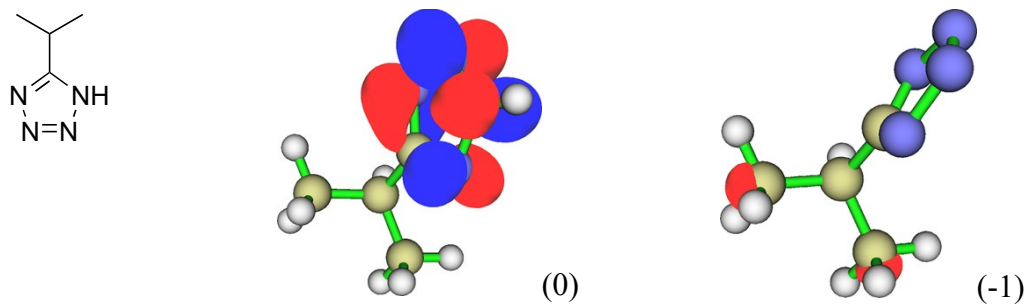
(0) (-1)

Figure S3 Chemical structure and LUMO isosurfaces of 5-isopropyl tetrazole in the neutral (0) and deprotonated form (-1).
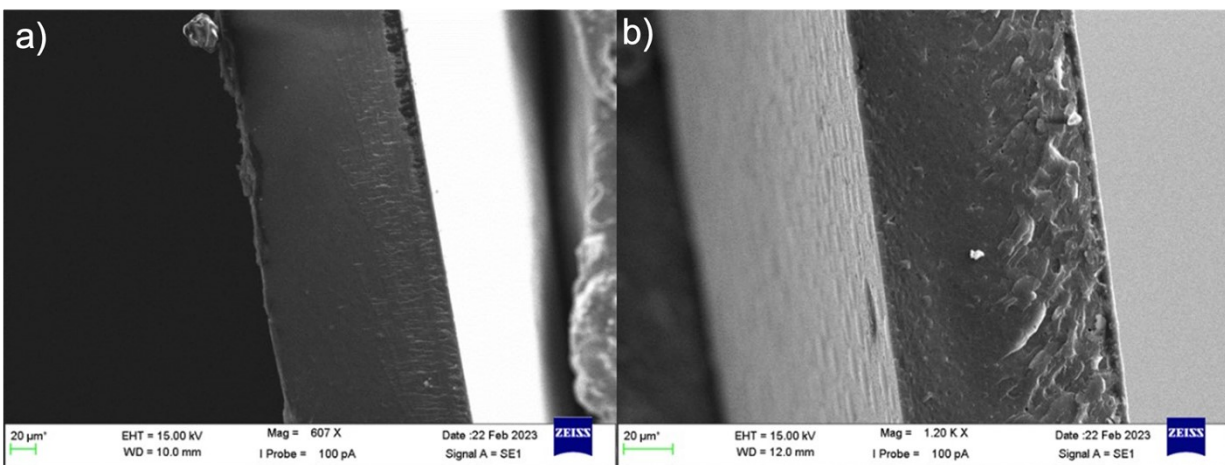
Figure S4 SEM micrographs of the cross-section of STz_{25} (a) and STz_{30} (b).
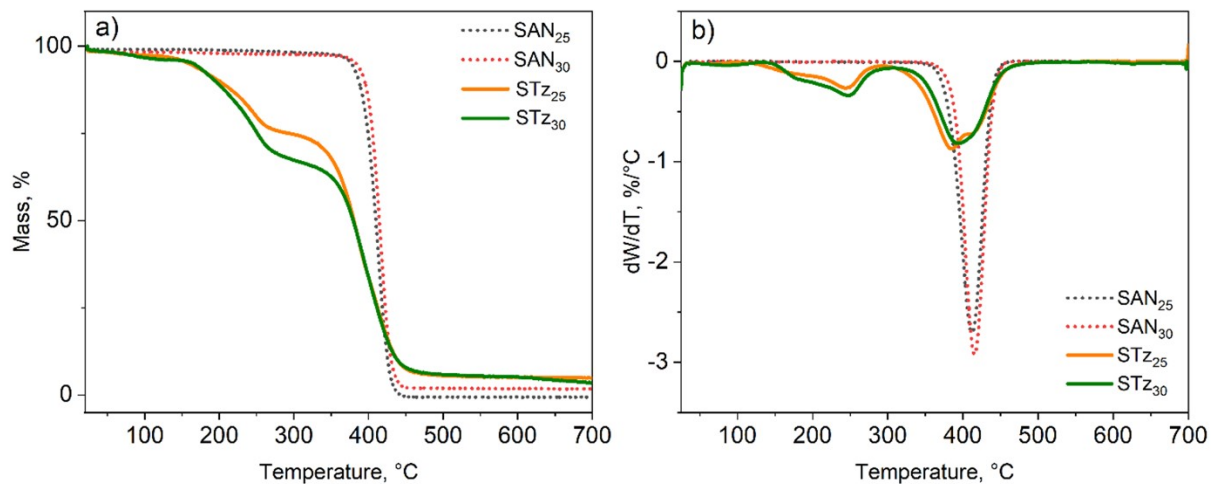
Figure S5 Thermogravimetric curves (a) and derivative of weight loss (b) of SAN_{25}/SAN_{30} polymers and STz_{25}/STz_{30}.
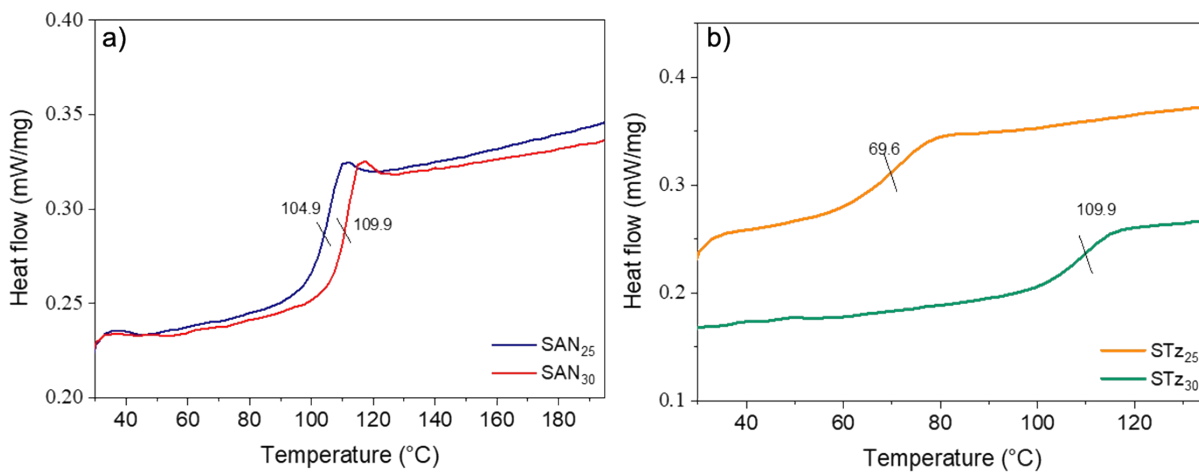
Figure S6 DSC curves of pristine polymers SAN_{25} and SAN_{30} (a) as well as tetrazolated STz_{25} and STz_{30} (b).
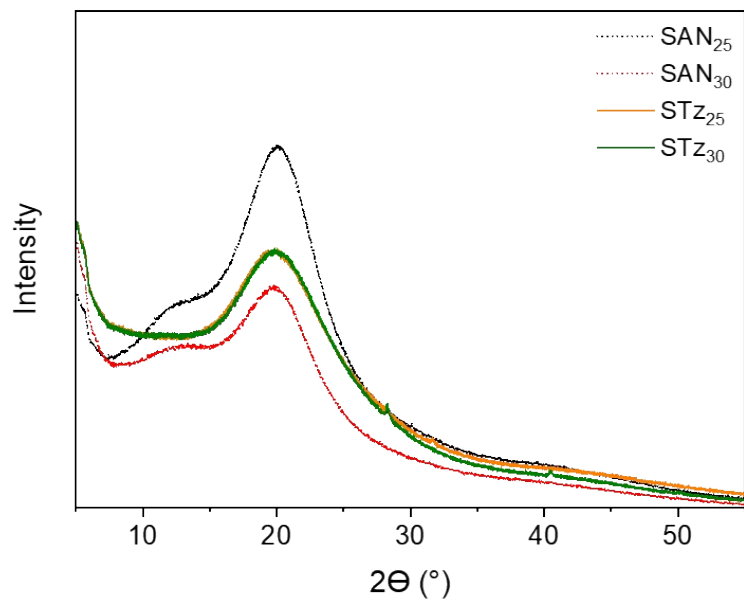
Figure S7 XRD curves of pristine SAN_{25}/SAN_{30} and STZ_{25}/STz_{30}.
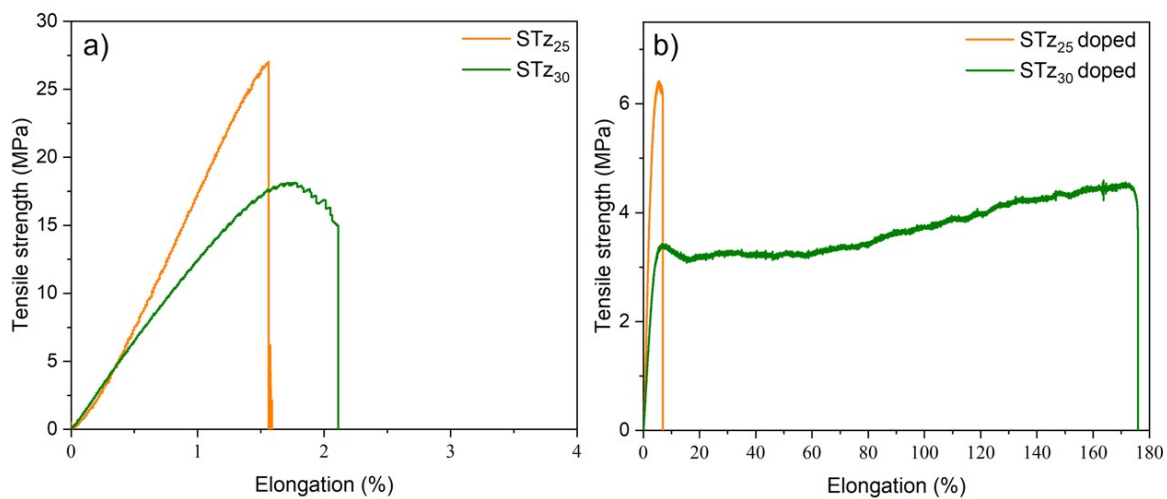
Figure S8 Representative stress-strain curves of pristine STZ_{25} and STz_{30} before (a) and after (b)

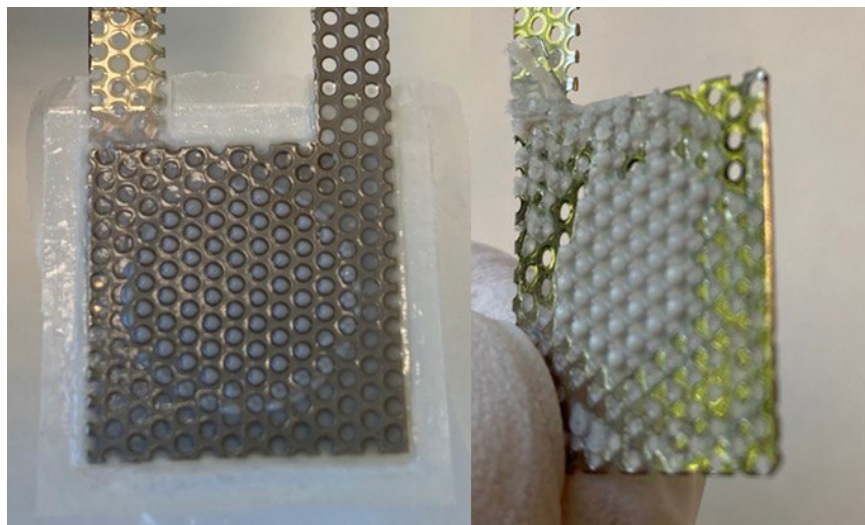equilibration in 15 wt% KOH.

Figure S9 Photographs of the STz$_{30}$ membrane after conductivity measurement at 60 °C.
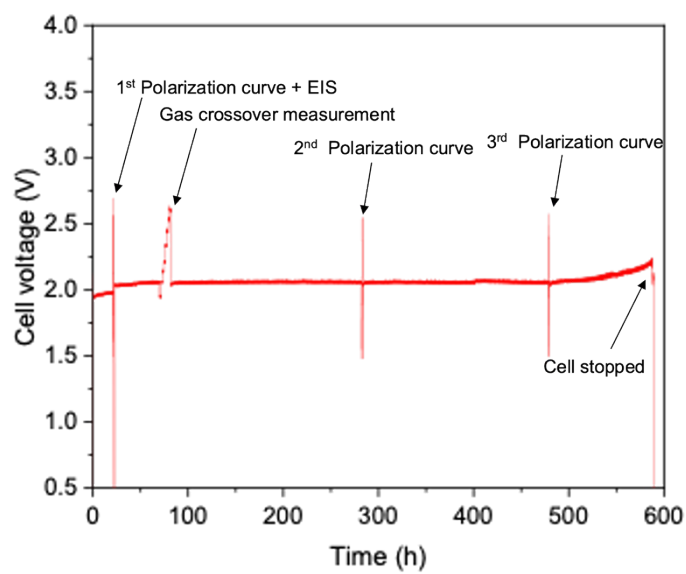

Figure S10 Time evolution of the cell voltage run at the constant current density of 100 mA cm^{-2} in 15 wt% KOH at 60 °C.
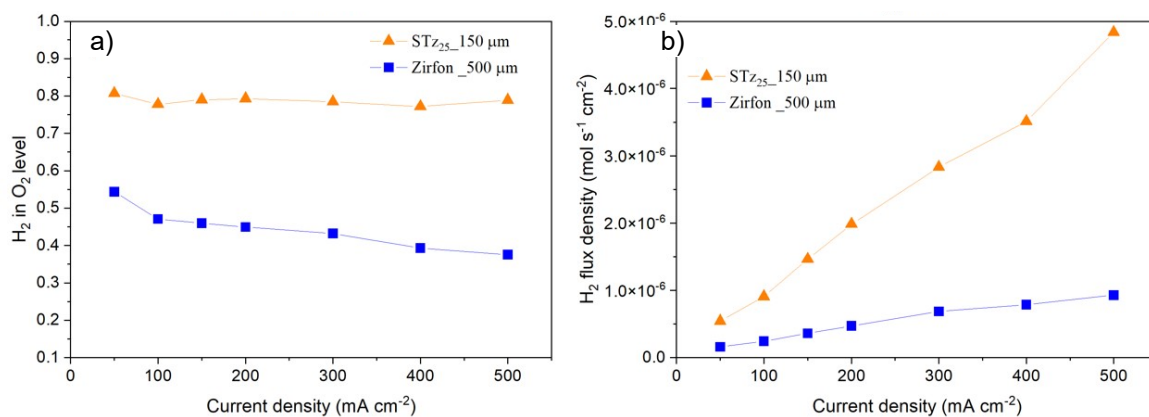
Figure S11 Nitrogen corrected H_2 in O_2 levels (a) and H_2 flux density (b) of STz_{25} and Zirfon at 60 °C in 15 wt% KOH.
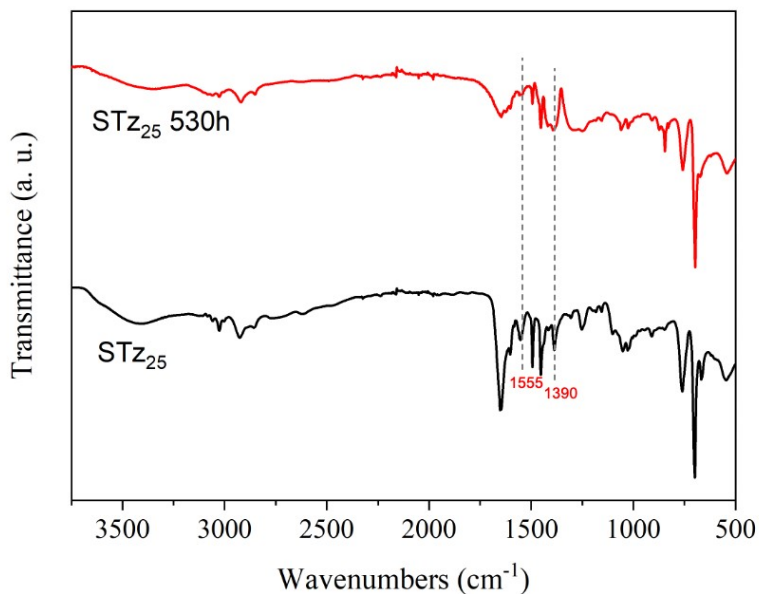

Figure S12 FTIR of STz_{25} before and after (STz_{25} 530 h) the electrolysis cell test at 60 °C in 15 wt% KOH for 530 hours.

Table S1 Mechanical parameters of STz$_{25}$ and STz$_{30}$ before and efter equilibration in 15 wt% KOH (at room temperature).

Membrane	Tensile strength (MPa)	Young's Modulus (MPa)	Elongation at break (%)
STz$_{25}$	27.0 ± 7.5	17.1 ± 2.4	1.5 ± 0.2
STz$_{25}$ doped	6.3 ± 0.6	1.6 ± 0.5	6.1 ± 0.7
STz$_{30}$	18.2 ± 2.2	11.9 ± 1.2	1.7 ± 0.1
STz$_{30}$ doped	3.3 ± 1.0	0.8 ± 0.1	8.2 ± 0.9

S3 Supplementary references

1   Y. Xia, S.C. Rajappan, D. Serhiichuk, M.R. Kraglund, J.O. Jensen, D. Aili, *J. Membr. Sci.* 2023, *680*, 121719.

2   J. Li, J. Wang, X. Chen, Z. Lv, T. Chen, T.A. Wang, *Solid State Ionics* 2014, **255**, 128-134.

3   R.A. Henry, *J. Am. Chem. Soc.* 1951, **73**, 4470.