Supporting Information

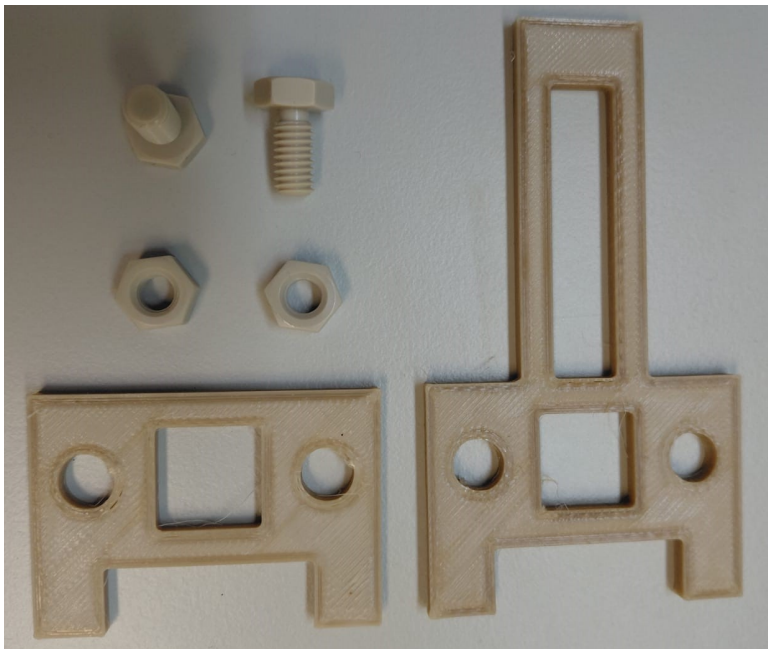

Fig. S1 | Custom-made membrane holder produced from PEEK via 3D printing. The membrane is positioned between the two larger plates, with a central cutout providing direct exposure to the Fenton reagent. PEEK screws and nuts secure the assembly, ensuring stable fixation of the membrane during testing.

Tab. S1 | Baseline membrane properties equivalent weight (EW) as provided by the supplier, ion exchange capacity (IEC) as calculated from the equivalent weight and the thickness of the pristine and 72 h degraded sample of the lsc- and ssc-PEM utilized in the accelerated stress test studies.

Parameter	**lsc-PEM**	**ssc-PEM**
EW* (g/equivalent)	1100 g eq^{-1}	980 g eq^{-1}
IEC (in milliequivalents/g)	0.909 meq g^{-1}	1.020 meq g^{-1}
Thickness** (µm)	Pristine: 199 µm After 72 h: 190 µm	Pristine: 104 µm After 72 h: 116 µm

*provided by the supplier.

**Thickness measured with foil thickness measuring tool (Käfer, Type 4 mm – 0.001 mm).

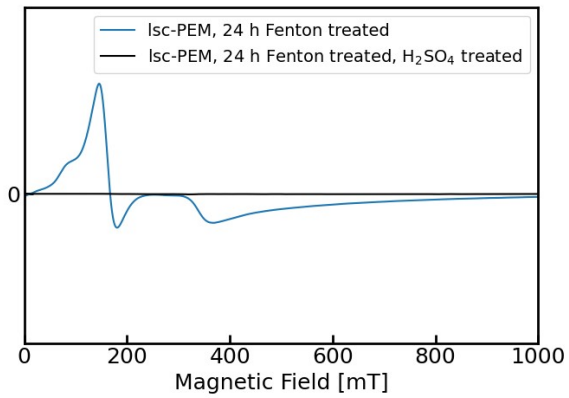

Fig. S2 | Continuous wave EPR-spectra of a lsc-PEM membrane after 24 h of Fenton treatment time (blue) and of the same sample after the post-treatment with 0.5 M H_2SO_4 (black).

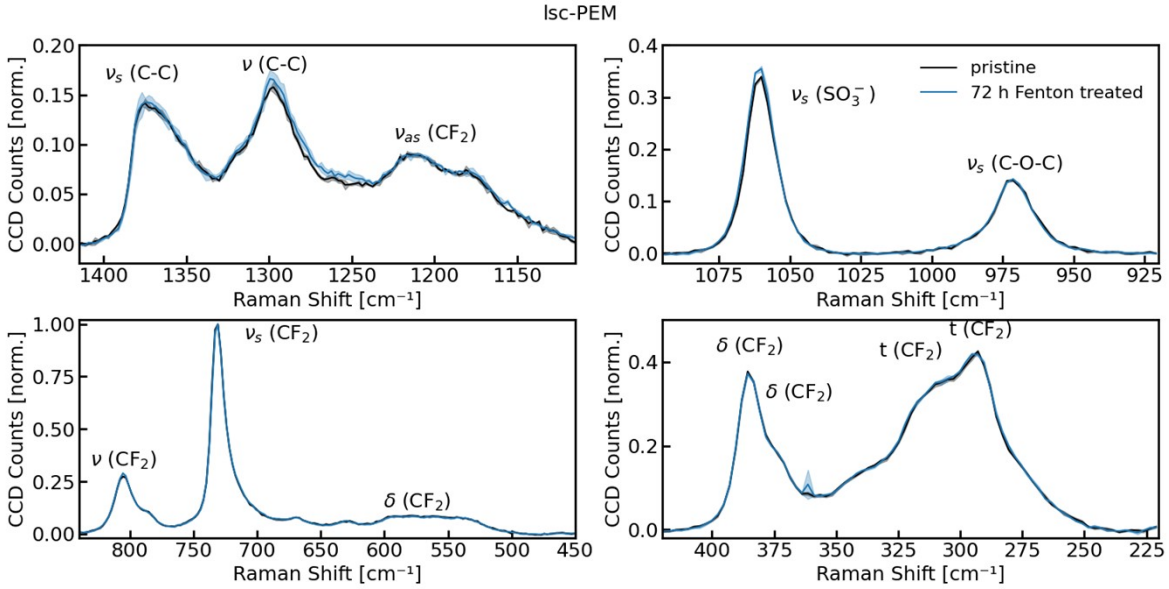

Fig. S3 | Normalized Raman spectra in the 225–1400 cm^{-1} range for a pristine and a 72 h Fenton treated lsc-PEM. Each spectrum was normalized to the $\nu_s(CF_2)$ symmetric-stretching band at 730 cm^{-1}. All symmetric-stretching vibration bands (ν_s), antisymmetric-stretching vibration bands (ν_{as}), twisting vibration bands (τ), and deformation vibration bands (δ) are indicated.

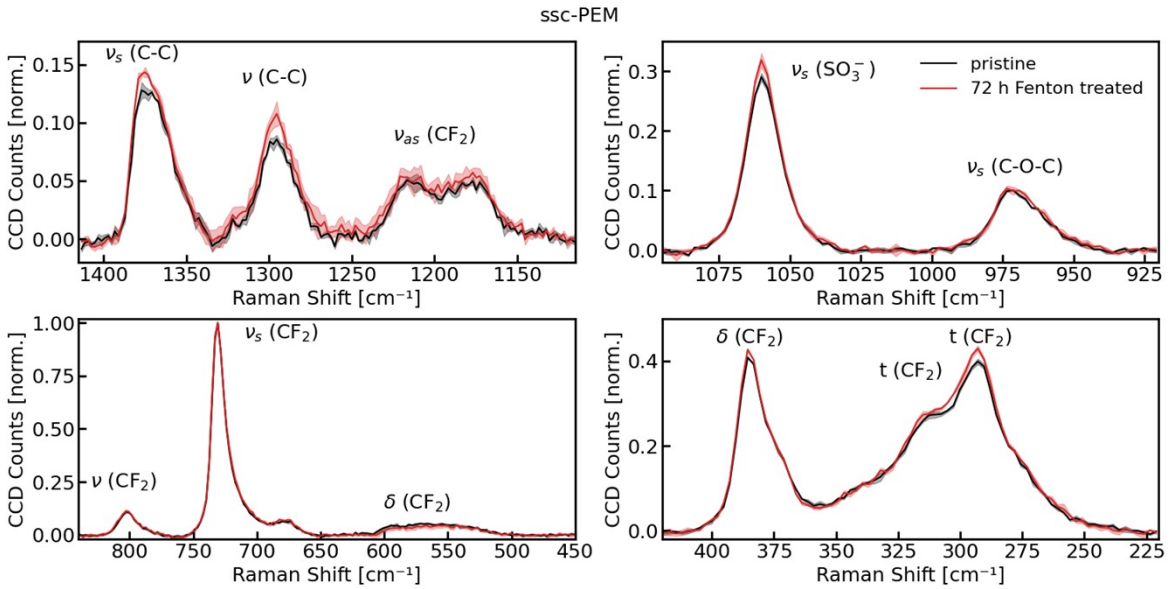

Fig. S4 | Normalized Raman spectra in the 225–1400 cm^{-1} range for a pristine and a 72 h Fenton treated ssc-PEM, with each spectrum normalized to the $\nu_s(CF_2)$ symmetric-stretching band at 730 cm^{-1}. All symmetric-stretching vibration bands (ν_s), antisymmetric-stretching vibration bands (ν_{as}), twisting vibration bands (τ), and deformation vibration bands (δ) are indicated.

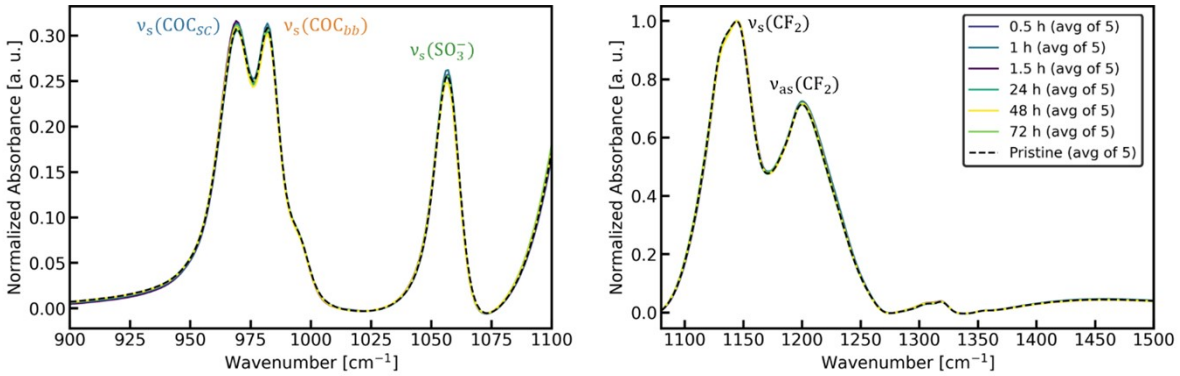

Fig. S5 | Averaged, normalized ATR-IR spectra of Nafion in the 900–1350 cm^{-1} range for pristine and Fenton treated lsc-PEMs (0.5, 1, 6, 24, 48, 72 h). Each spectrum represents the average of five measurements and was normalized to the $\nu_s(CF_2)$ symmetric-stretching band at 1143 cm^{-1}. Side chain vibrational bands at 969 cm^{-1} (COC symmetric-stretch), 982 cm^{-1} (lsc-PEM-specific COC symmetric-stretch), and 1056 cm^{-1} (SO_3^- symmetric-stretch) are indicated.

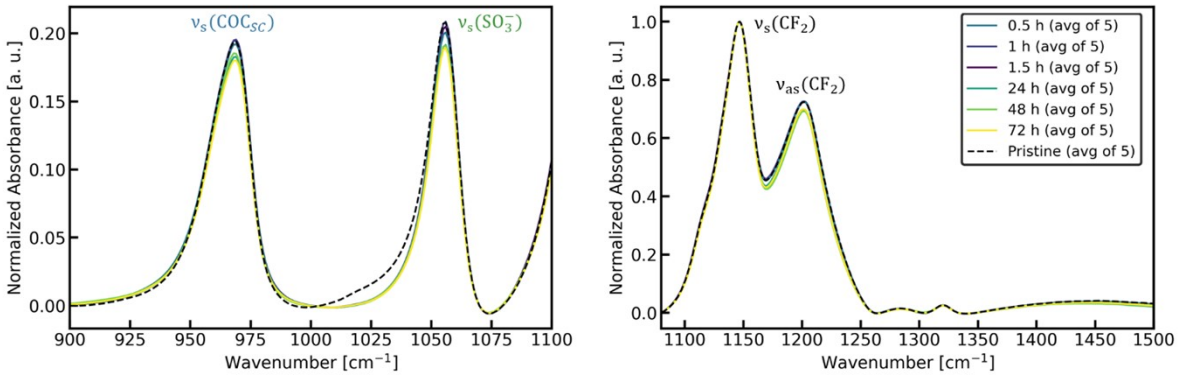

Fig. S6 | Averaged, normalized ATR-IR spectra of Nafion in the 900–1350 cm^{-1} range for pristine and Fenton treated ssc-PEMs (0.5, 1, 6, 24, 48, 72 h). Each spectrum represents the average of five measurements and was normalized to the $\nu_s(CF_2)$ symmetric-stretching band at 1143 cm^{-1}. Side chain vibrational bands at 969 cm^{-1} (COC symmetric-stretch) and 1056 cm^{-1} (SO_3^- symmetric-stretch) are highlighted.

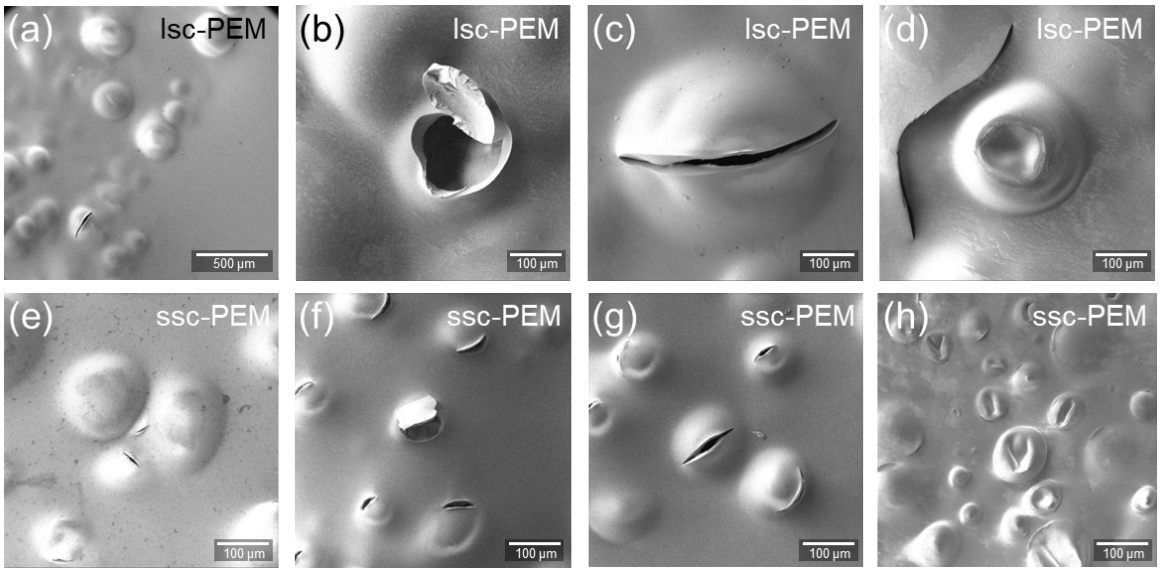

Fig. S7 | SEM images showing representative surface morphologies formed on lsc-PEM (a–d) and ssc-PEM (e–h) after Fenton treatment. Four characteristic features are observed in both membrane types: intact rounded blisters (a, e), burst-cap blisters (b, f), slit-like tears (c, g), and collapsed "volcano" structures (d, h). These features appear in increasing numbers with longer exposure, reflecting progressive blistering and surface deterioration.

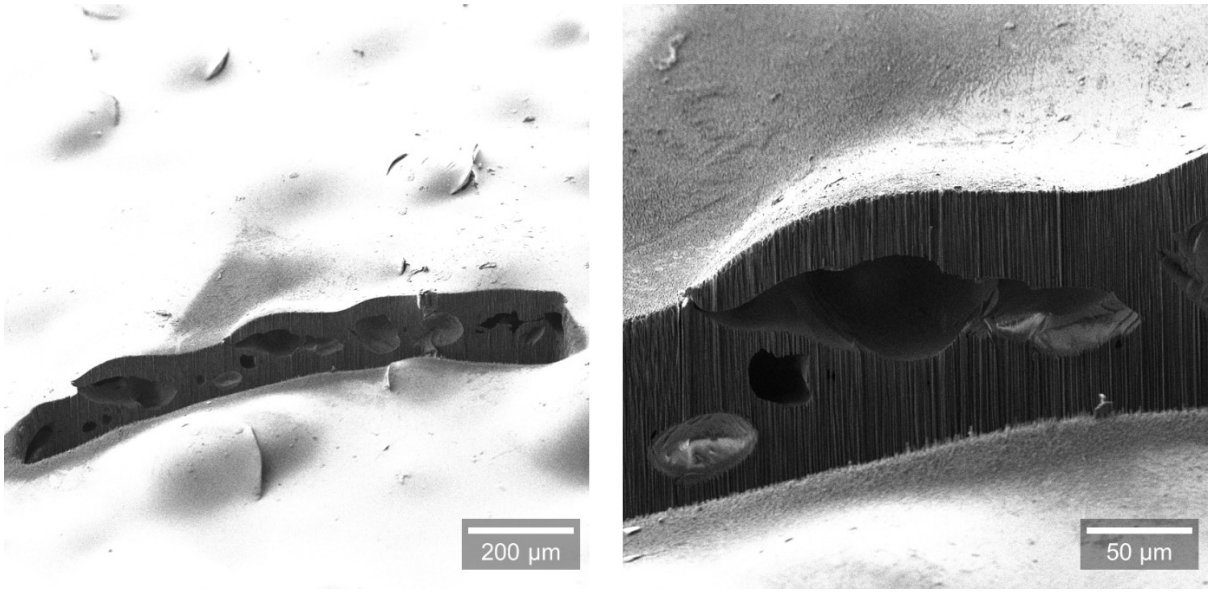

Fig. S8 | Cross-sectional SEM images of lsc-PEM after 24 h of Fenton treatment, showing voids beneath surface protrusions.

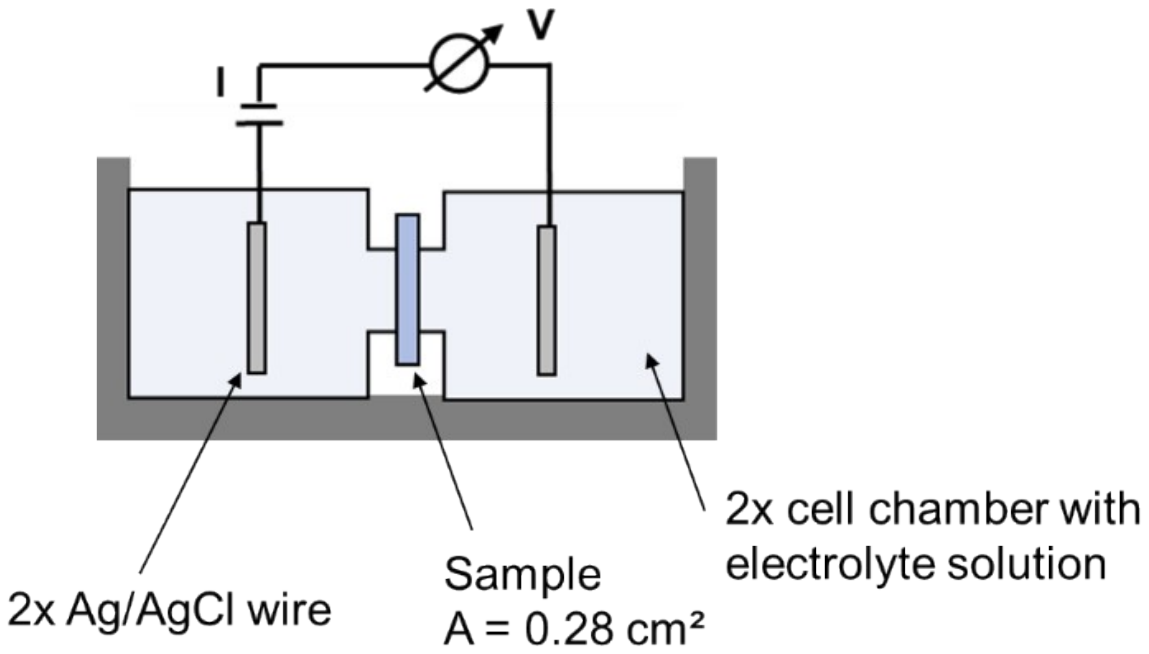

Fig. S9 | Schematic illustration of the electrochemical cell used for I–V measurements. The membrane is fixed between two cell compartments, and the transmembrane ion current is measured at a 0.28 cm^2 sample area exposed to 100 mM H_2SO_4 electrolyte solution.

Table S2 | Characterization techniques applied to Fenton treated proton exchange membranes (PEMs), the type of structural or chemical insight provided, and the corresponding observations reported in the literature.

Technique		General Insight	Observations in Fenton Treated Membranes
NMR (^{19}F MAS, ^{13}C solid-state and solution-state)	Molecular-level insight into main chain vs. side chain degradation pathways	Dissensus in literature on selective side-chain degradation with intact backbone[31,37] versus concurrent degradation of both under prolonged exposure[35]	
ATR-FTIR		Probes specific bond vibrations (e.g., C–F, C–O–C, SO_3)	Conflicting literature results: preferential side chain degradation[39,40] versus insignificant spectral changes[32,41,42]
SEM		Visualizes surface and internal	Consistent report on surface

	morphology	roughening, void formation, and pinhole development indicative of severe morphological degradation[32,39,43–45]

Superscript numbers indicate literature sources cited in the introduction.

Table S3 | SAXS/WAXS features observed in pristine lsc-PEM and ssc-PEM membranes.

Peak name	**Correlates to**	**lsc-PEM**		**ssc-PEM**	
		q [Å^{-1}]	*d*-spacing [Å]	*q* [Å^{-1}]	*d*-spacing [Å]
Matrix knee	intercrystalline distance[61,68]	0.058	108	0.056	112
Ionomer peak	hydrophilic *d*-spacing[61,68]	0.22	28.6	0.27	23.3
WAXS 1	intermolecular chain spacing[68,69]	1.20	5.2	1.20	5.2
WAXS 2	intramolecular distances[69]	2.75	2.3	2.75	2.3

The table lists the main peaks in the low-*q*, intermediate-*q*, and high-*q* regions and their corresponding structural correlations.

Table S4 | Summary of changes in SAXS features for lsc-PEM and ssc-PEM after Fenton treatment.

Membrane	**Observation**	**Correlates to**	***q* [Å^{-1}]**	***d*-spacing [Å]**
lsc-PEM	Shift of Ionomer peak	Hydrophilic-domain spacing[61,68]	0.22 → 0.24	28.6 → 26.2
ssc-PEM	Evolving low-q upturn at ~ 0.003 Å^{-1} (30, 90 min)	Polymeric aggregates[69]	~ 0.003	~ 2100
lsc-/ ssc-PEM	Decreasing matrix knee intensity	intercrystalline distance[61,68]	~ 0.05	~ 110

The table highlights shifts in ionomer peaks, variations in low-*q* scattering, and attenuation of the matrix knee.

Table S5 | Water contact angles (ϑ) of pristine and Fenton treated lsc-PEM and ssc-PEM.

Membrane	**Fenton Treatment [h]**	**Contact Angle, ϑ [°]**	**± SD [°]**
lsc-PEM	0	106.68	2.49
	1	89.55	3.67
	6	86.93	6.93
ssc-PEM	0	94.78	4.79
	1	82.87	6.92
	6	93.76	5.81

Data are reported as mean ± standard deviation (SD).

Table S6 | Adhesion forces (F) for water droplets on pristine and Fenton treated lsc-PEM and ssc-PEM.

Membrane	**Fenton Treatment [h]**	**F_{H2O} [µN mm^{-2}]**	**± SD_{H2O} [µN mm^{-2}]**
lsc-PEM	0	197.89	1.15
	1	239.06	6.96
	6	240.95	2.18
ssc-PEM	0	207.58	9.42
	1	204.02	10.46
	6	211.33	3.44

Data are reported as mean ± standard deviation (SD).