Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting information for

Efficient Toluene Barrier Membrane for High-Performance Direct Toluene Hydrogenation via an Electrochemical Process

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Degree of sulfonation (DS) determination of SPAES PEM.

The DS of the synthesized SPAES was evaluated through ^{1}H NMR analysis (Bruker DRX500 spectrometer, 500 MHz) following the dissolution of the ionomers in DMSO-d_6 as a solvent. The DS for the SPAES was determined as follows: DS (%) = n / (n + m) × 100 (%). The values for n and m were determined through integration of the ^{1}H NMR spectra. This determination was based on the following correlation: $(H_1 + H_2 + H_3)/(H_4 + H_5 + H_6 + H_7 + H_8 + H_9) = 6n / (8n + 16m)$, where $H_\#$ represents the integration value of specific peaks in the ^{1}H NMR spectra (Figure S1). Therefore, DS of the synthesized SPAES, prepared with varying ratios of hydrophilic/hydrophobic monomers, was calculated to be 37.3%, 48.3%, and 57.2% respectively. Based on the calculated DS, the SPAES PEMs were named SPAES40, SPAES50, and SPAES60, respectively.

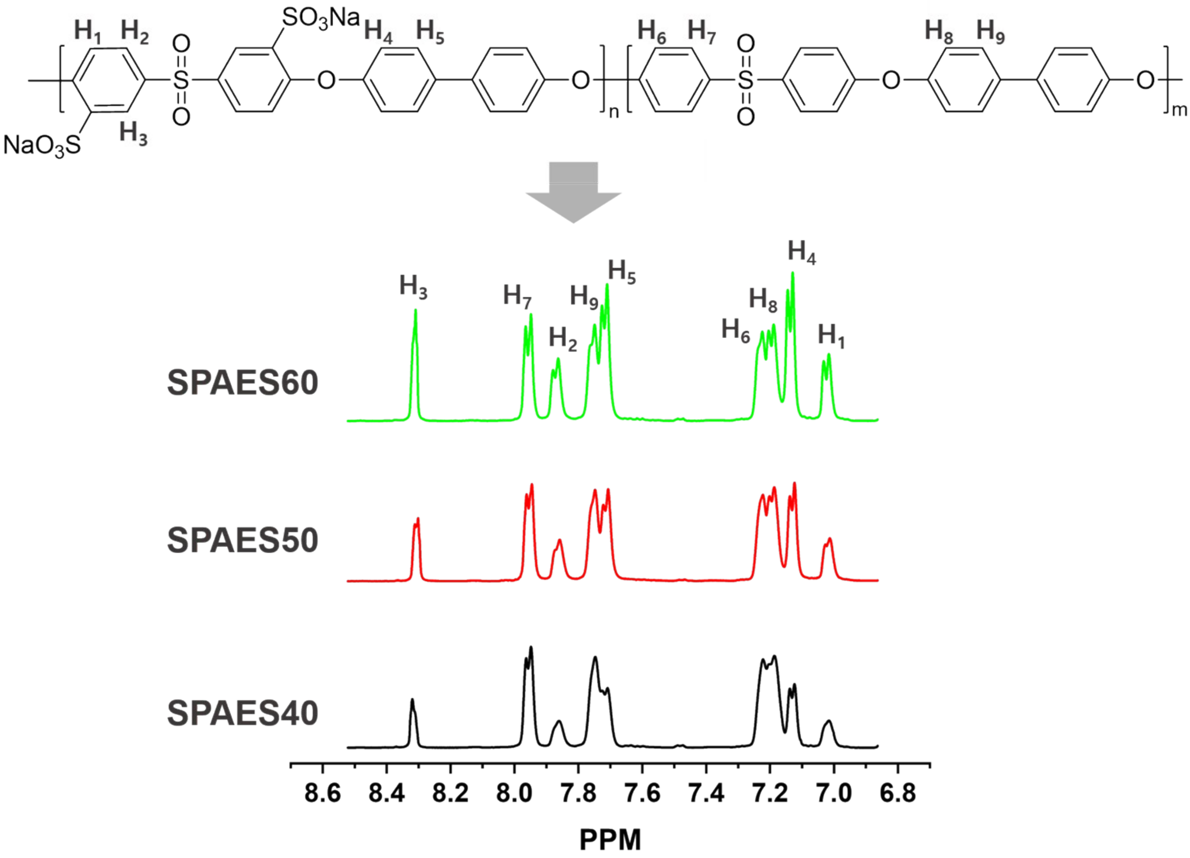

Figure S1. Chemical structure and ^{1}H NMR spectra of SPAES40, SPAES50, and SPAES60.

Table S1. The number-average molecular weight (M_n), weight-average molecular weight (M_w), dispersity ($Đ$), proton conductivity (σ) of the synthesized SPAES series.

Membrane	M_n (kg/mol)	M_w (kg/mol)	$Đ$	σ^a (mS/cm)
SPAES40	169.8	326	1.92	64
SPAES50	142.6	255.3	1.79	102
SPAES60	160.9	304.1	1.89	125
Nafion 212	N/A	N/A	N/A	68

[a] The proton conductivity measured at 25 °C in water.

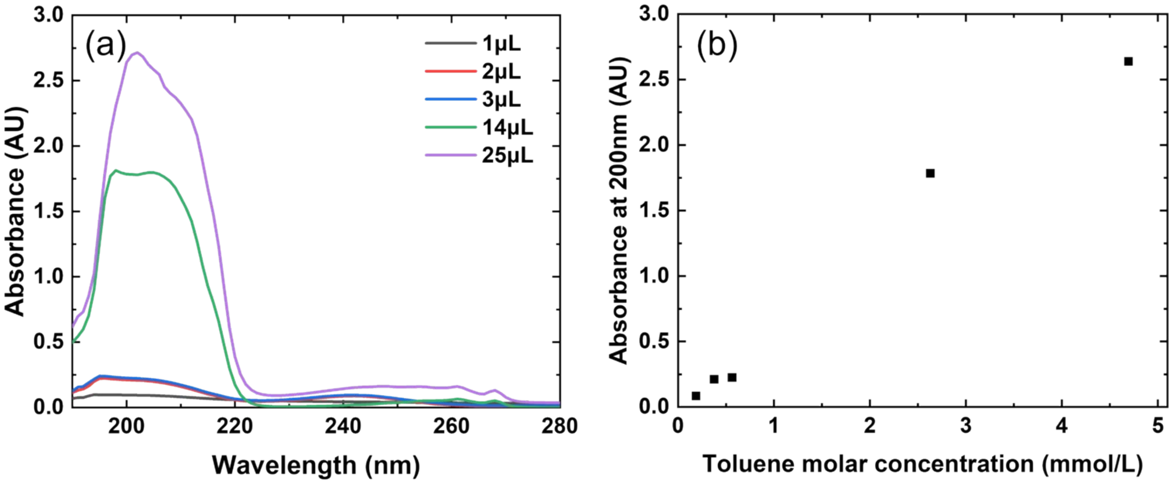

Figure S2. (a) Absorption spectra of toluene at varying concentrations in a 50 mL 1M H_2SO_4 solution. (b) Calibration curve correlating absorbance with toluene concentration in a 1M H_2SO_4 solution.

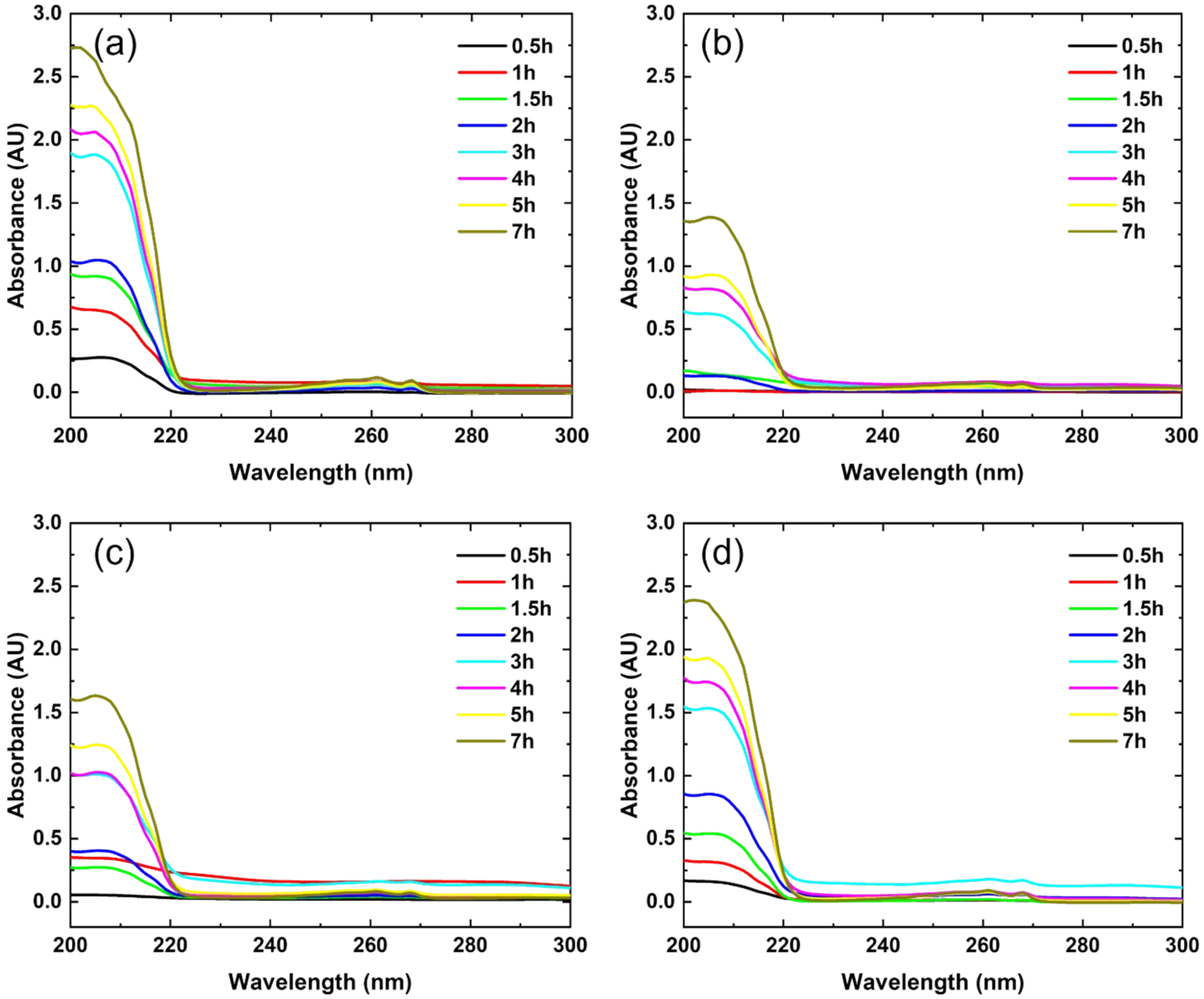

Figure S3. UV spectra corresponding to the changes in toluene concentration on the toluene-deficient side (1M H_2SO_4 solution compartment) of a diffusion cell with (a) Nafion, (b) SPAES40, (c) SPAES50, and SPAES60.

Determination of toluene permeability through the PEM

The permeation mechanism of toluene is considered to be diffusion-driven by concentration gradient differences within the membrane. Therefore, to calculate the permeability of toluene passing towards the sulfuric acid solution, Fick's first law of diffusion, as represented by equation (S1), was employed.

$$J = D \times (C_1 - C_2) / l, \tag{S1}$$

where, J is the toluene flux in the membrane, D is the toluene diffusion coefficient, C_1 is the toluene solubility within the membrane, C_2 is the concentration of toluene that has permeated through the PEM over time, l is the membrane thickness, respectively. Concentrations C_1 and C_2 within the membrane are determined by the partition coefficient (K) multiplied by the toluene concentration (C_T) in the chamber and by the permeated toluene concentration in the sulfuric acid solution over time (C_S), respectively, represented C_1=KC_T and C_2=KC_S. Therefore, equation (S2) is written as follows,[S1]

$$J = D \times (KC_\mathrm{T} - KC_\mathrm{S}) / l, \tag{S2}$$

The rate of change in toluene concentration (C_S) within the sulfuric acid over time can be expressed as $V \times (\mathrm{d}C_\mathrm{S} / \mathrm{d}t)$, where V represents the volume of sulfuric acid. The total amount of toluene passing through the membrane per unit time is denoted as $J \times A$, where A is the effective area of the membrane. Therefore, by combining the rate of change in toluene concentration within the sulfuric acid chamber with the toluene permeation flux through the membrane, the equation is represented as follow,

$$V \times (\mathrm{d}C_\mathrm{S} / \mathrm{d}t) = J \times A, \tag{S3}$$

Using equations (S2) and (S3), equation (S4) is derived by solving for C_S,

$$C_S = C_T(1-\exp(-(P \times A) / (l \times V) \times t)), \tag{S4}$$

The derived equation S4 is represented as a graph in the form of $y = C_T(1-\exp(-kt))$, from which the toluene permeability ($P = D \times K$) was obtained.

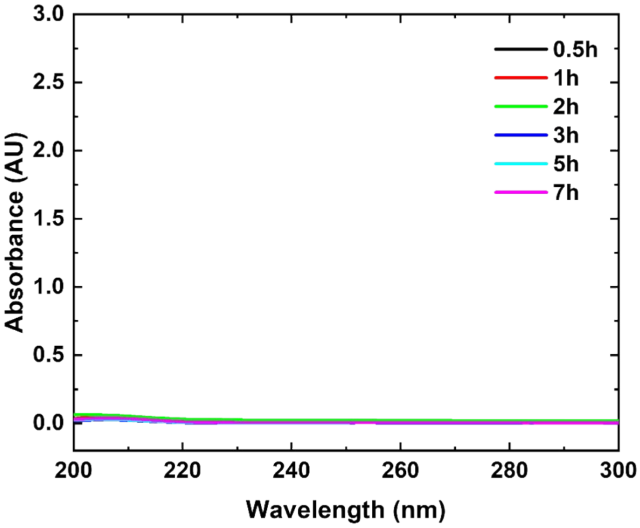

Figure S4. UV spectra corresponding to the changes in toluene concentration on the toluene-deficient side of the diffusion cell with PTFE film.

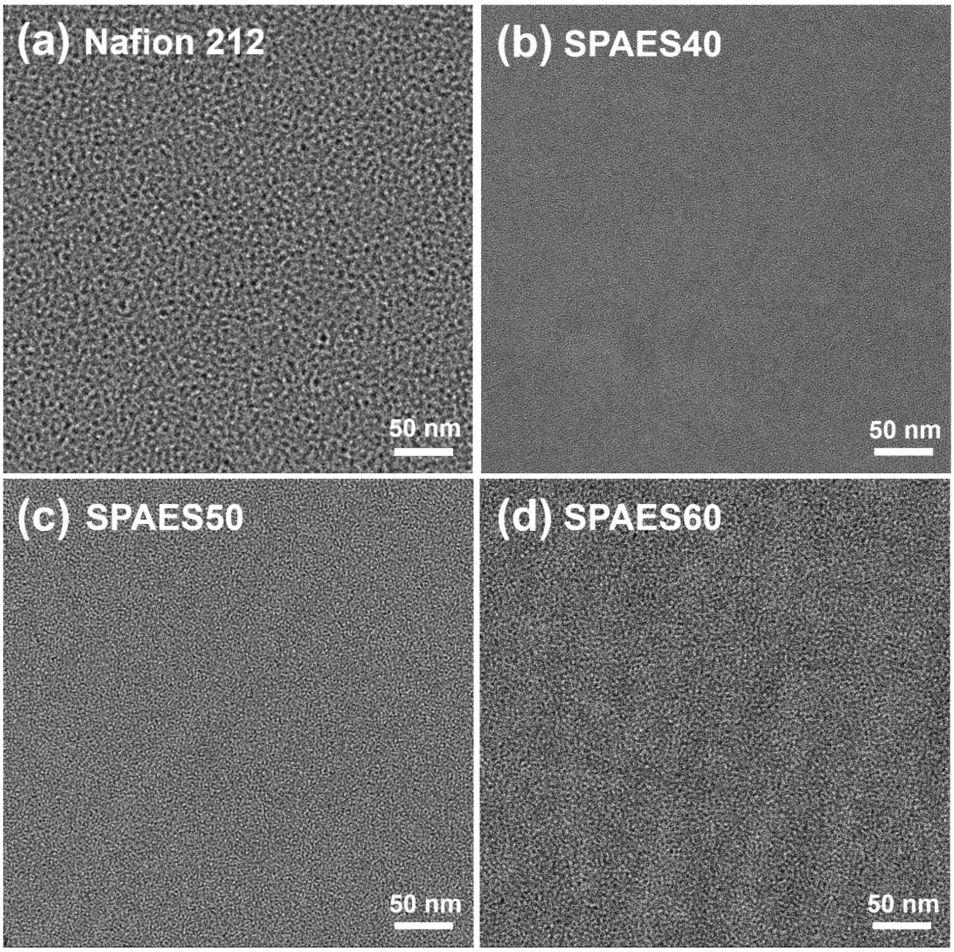

Figure S5. Cross-sectional TEM images of (a) Nafion 212, (b) SPAES40, (c) SPAES50, and (d) SPAES60. Scale bar: 50 nm.

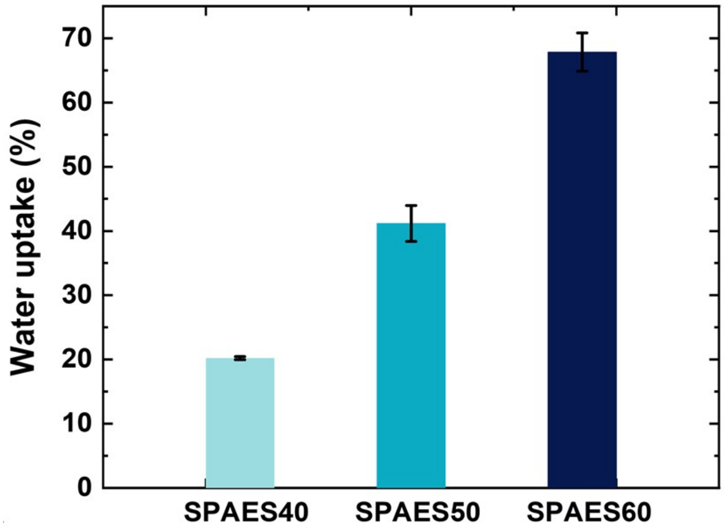

Figure S6. Water uptake of SPAES PEMs as a function of DS at 25 °C.

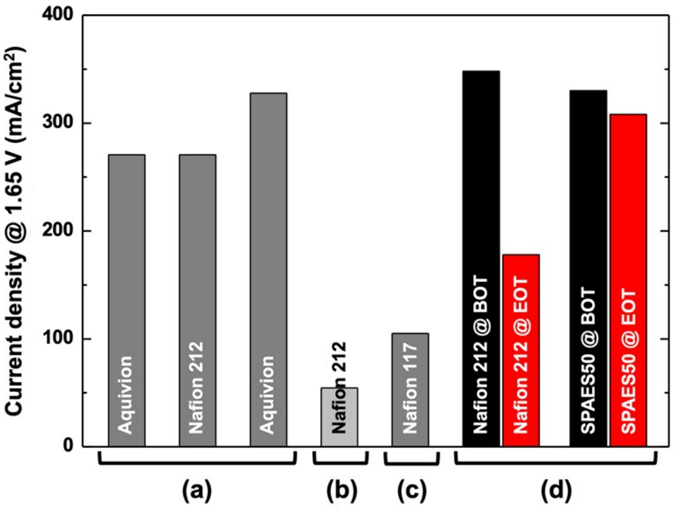

Figure S7. The summary of DEHT current density at 1.65 V; (a) Aquivion, Nafion 212, and Aquivion PEMs with Nafion, Nafion, and Aquivion ionomers for the electrodes, respectively, at 60 °C,[S2] (b) Nafion 212 with Nafion ionomers for the electrodes at 60 °C,[S3] (c) Nafion 117 with Nafion ionomers for the electrodes at 60 °C,[S4] (d) Nafion 212 and SPAES50 with Nafion ionomers for the electrodes at BOT and EOT of the test at 25 °C in this study. Only results with 100% toluene feed for the cathode were included for consistency.

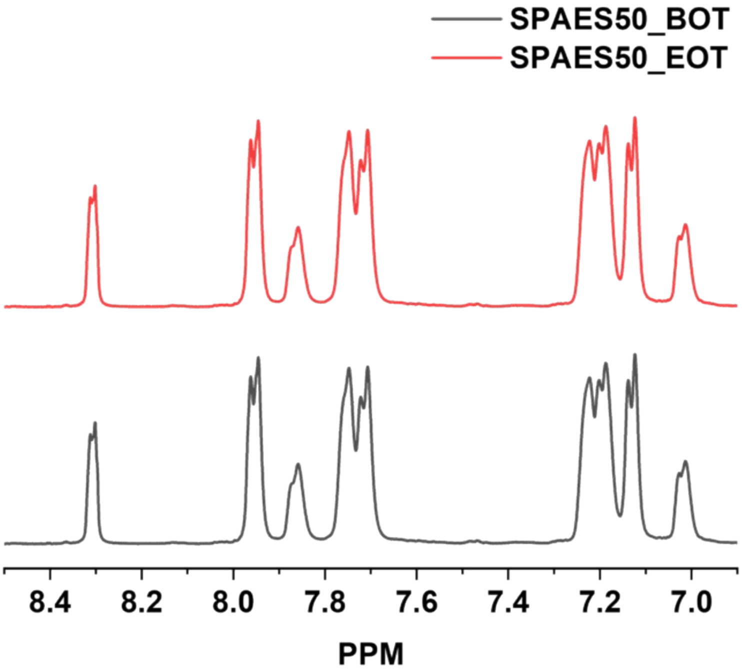

Figure S8. The ^{1}H NMR spectra of SPAES50 before (BOT) and after (EOT) 48 hours of operation at a constant current density of 150 mA/cm^2.

Table S2. Molecular weights and DS values of SPAES50 before (BOT) and after (EOT) 48 hours of operation at a constant current density of 150 mA/cm^2.

Condition	M_n (kg/mol)	M_w (kg/mol)	$Đ$	DS (%)
BOT	142.6	255.3	1.79	48.3
EOT	134.7	250.1	1.86	48.0

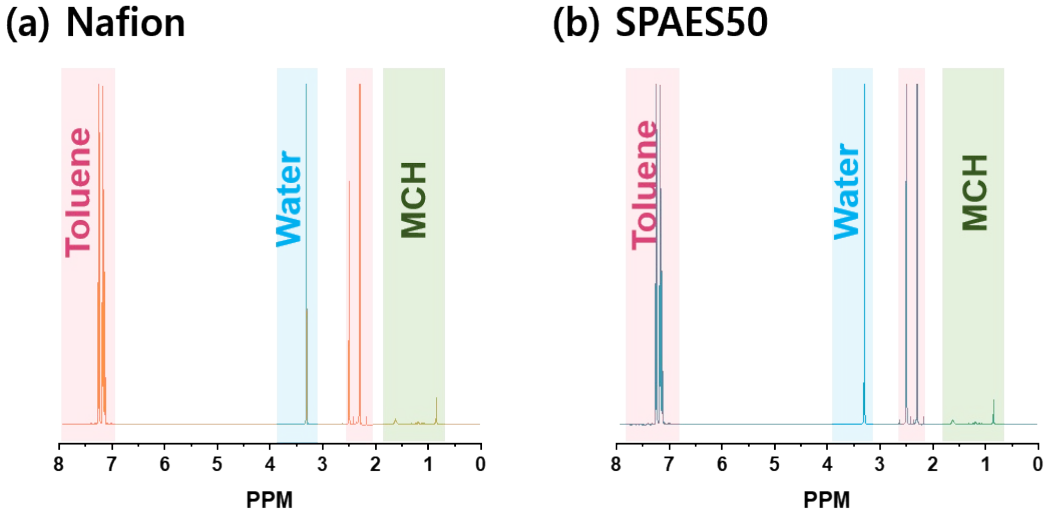

Figure S9. ^{1}H NMR results on the anode supply solution (1M sulfuric acid solution) after durability test.

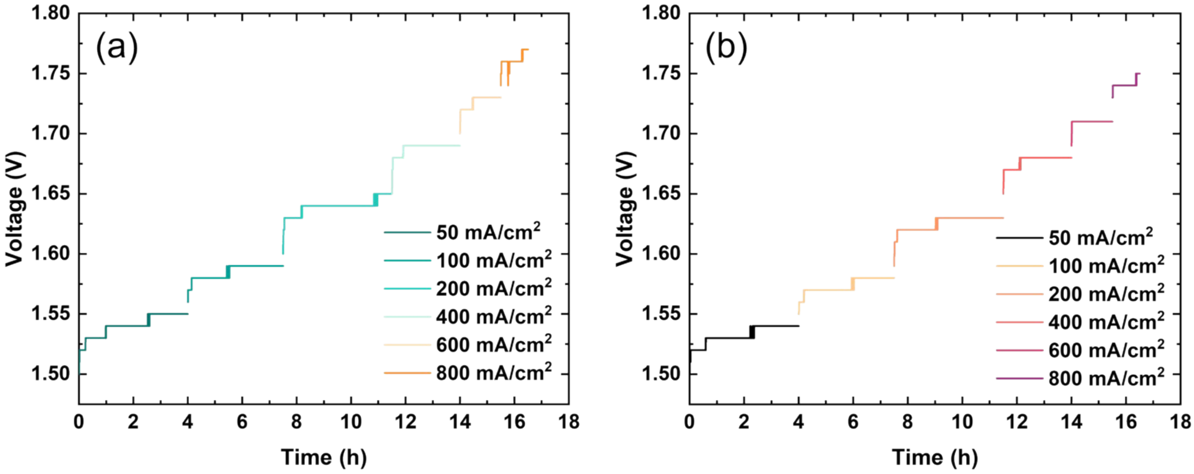

Figure S10. The voltage profile changes of DEHT cells with (a) Nafion and (b) SPAES50 PEMs at various current densities.

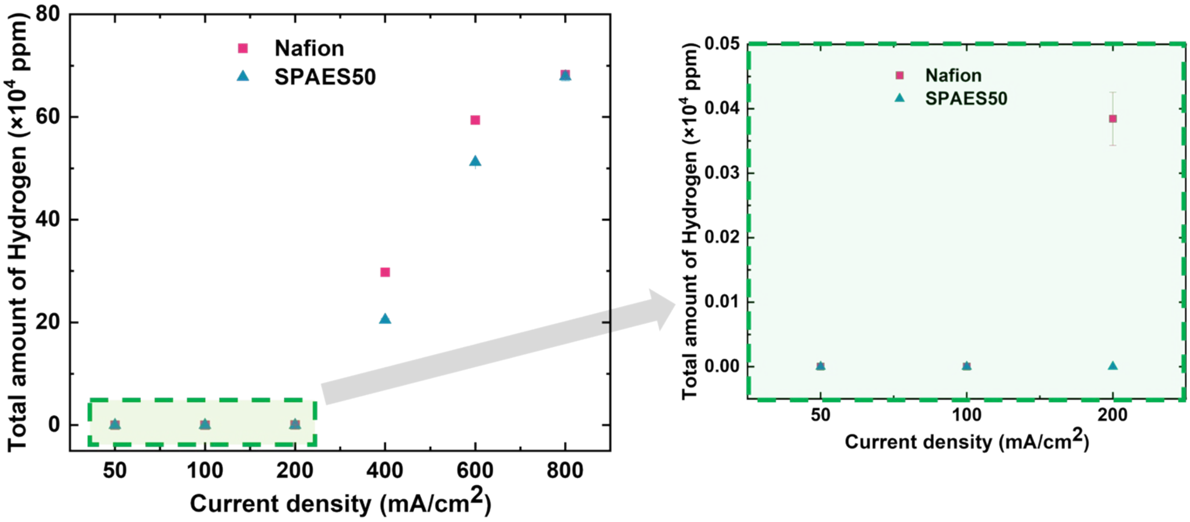

Figure S11. The total amount of hydrogen quantified by GC chromatography over a specific time.

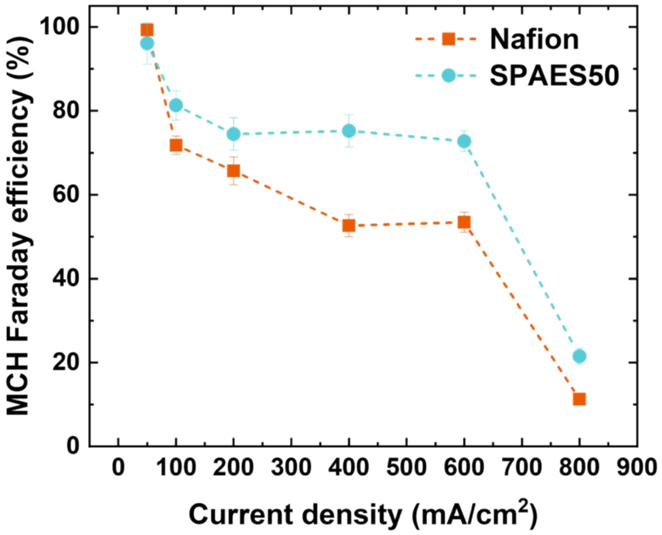

Figure S12. The MCH Faraday efficiency of DEHT cell with Nafion and SPAES PEM calculated using ^{1}H NMR spectra.

References

S1. S. Bukola, Z. Li, J. Zack, C. Antunes, C. Korzeniewski, G. Teeter, J. Blackburn and B. Pivovar, *J. Energy Chem.*, 2021, **59**, 419–430.D.

S2. K. Nagasawa, K. Tanimoto, J. Koike, K. Ikegami and S. Mitsushima, *J. Power Sources*, 2019, **439**, 227070.

S3. S. Mitsushima, Y. Takakuwa, K. Nagasawa, Y. Sawaguchi, Y. Kohno, K. Matsuzawa, Z. Awaludin, A. Kato and Y. Nishiki, *Electrocatalysis*, 2015, **7**, 127–131.

S4. K. Nagasawa, A. Kato, Y. Nishiki, Y. Matsumura, M. Atobe and S. Mitsushima, *Electrochim. Acta*, 2017, **246**, 459–465.