Supporting Information

High-performance ultrathin perfluorinated sulfonic acid membranes with

thermo-morphology control for a vanadium redox flow battery

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Discussion S1. Molecular structure of PFSA ionomers



Figure S1. a) Molecular structure of PFSA ionomer and b) schematic images and the number of TFE repeating unit (*n*) of EW1000 and EW1100. The *n* is calculated by Equation S1 (MW_{TFE} unit : 100.02 g mol⁻¹, MW_{side chain} : 443.97 g mol⁻¹).

PFSA ionomers are composed of a hydrophobic PTFE backbone and hydrophilic sulfuric acid side chains (**Figure S1**). Due to these structural features, the PFSA ionomer has amphiphilic properties and can be effectively adsorbed on the interface, forming a stable monolayer at the air/water interface with a small amount of PFSA dispersion.^{1–6} In particular, the interfacial properties of the PFSA monolayer depend on the molecular structure of the PFSA ionomer, which affects not only the packing structure but also the formation and stability of the monolayer on the interface.⁷ Generally, when the side chain lengths are the same, the PFSA ionomer is classified by its equivalent weight (EW), which is defined as the weight of the PFSA ionomer per mole of SO₃H. EW is represented as **Equation S1**,

EW
$$[g \text{ mol}^{-1}] = n \times MW_{\text{TFE unit}} + MW_{\text{side chain}}.$$
 Equation S1

where $MW_{TFE unit}$ and $MW_{side chain}$ are the molecular weight of tetrafluoroethylene (TFE) repeating unit and side chain, respectively, and *n* is the number of TFE units (**Figure S1a**).

The number of TFE units determines the length between the sulfuric acid side chains, which affects the ionic conductivity and mechanical properties of the PFSA ionomer membrane. In this study, two PFSA ionomers with EWs of 1100 g mol⁻¹ and 1000 g mol⁻¹, respectively, were used to investigate the molecular structure effect of PFSA ionomers on the nanomorphology and ion transport properties of ultrathin membranes. The number of TFE units in each PFSA ionomer is ~6 for Nafion 1000 and ~7 for Nafion 1100, indicating that Nafion 1100 has a longer backbone between the side chains (**Figure S1b**).

Discussion S2. Absorption behavior of PFSA ionomers on the air/water interface

PFSA ionomers can be easily absorbed on the air/water interface to form the stable monolayer because of the hydrophobic polytetrafluoroethylene (PTFE) backbone and hydrophilic sulfonic acid side chain.^{1–6} However, the surface activity and absorption behavior of PFSA ionomers at the air/water interface are highly reliant on their molecular structure.⁷ To investigate the absorption behavior of ionomers, two kinds of commercial PFSA ionomer dispersions, i.e., NafionTM D521 (EW: 1100 g mol⁻¹ of SO₃H) and NafionTM D520 (EW: 1000 g mol⁻¹ of SO₃H) was used. Each PFSA ionomer dispersed in solution has different EW, but has same side chain length. Given that the EW is defined as polymer grams per one mole of sulfuric acid, higher EW has more TFE repeat units. Therefore, ionomer dispersed in NafionTM D521 has longer backbone between side chains than that of ionomer dispersed in NafionTM D520 (**Figure S1** and **Discussion S1**), and each ionomer is denoted as EW1100 and EW1000 according to their EWs.

In order to introduce the ionomers on the air/water interface, PFSA dispersion was directly spread on the interface using the microsyringe. In addition, pH 2 of HCl aqueous solution was utilized as subphase to increase the absorption efficiency of ionomer on the interface by charge screening effect during direct spreading of dispersion.⁶ To examine the

absorption behavior of each PFSA ionomer, each 1 μ L of dispersion was loading onto air/HCl aqueous solution interface, and the change of surface pressure (Π) was observed. At each loading step of dispersion, the dispersion solvent was sufficiently evaporated for at least 3 minutes for stable Π (**Figure S2a** and **Figure S3a**).



Figure S2. Schematic images of a) preparation of densely packed PFSA Langmuir monolayer with aligned structures and b) deposition of the monolayer by Langmuir-Blodgett method on the substrate.



Figure S3. a) Surface pressure (Π) measurements of each PFSA ionomer on the air/HCl aqueous solution (pH 2) interface according to spreading amounts and b) Surface pressure-area (Π -A) isotherm of each PFSA Langmuir monolayer on the air/water interface. The trough area is 243 cm², and Π increases as increasing spreading amounts on the interface. The trough area was saturated with ~ 10 µL of the each PFSA ionomer dispersion, and EW1000 showed the highest Π (Π ~ 44 mN m⁻¹) after saturation. After evaporation of dispersion solvent for 5 minutes when Π reached the saturation value by dispersion spreading, the monolayer on the interface was compressed by physical barriers at the rate of 5 mm min⁻¹.

As shown in **Figure S3a**, Π of all PFSA ionomers increased as increasing the amount of spreading, and the whole interface area (243 cm²) was saturated with about 10 µL of dispersion solution in all PFSA ionomers. The Π at saturation (Π_{sat}) was saturated at $\Pi_{sat} \sim 42$ mN m⁻¹ for EW1100 and $\Pi_{sat} \sim 44$ mN m⁻¹ for EW1000, and EW1000 showed higher Π than that of EW1100. PFSA ionomers dispersed in an aqueous solution are absorbed onto the interface due to their surface activity and form the monolayer on the air/water interface spontaneously. Therefore, the Π depends on the surface activity of the PFSA ionomer. In general, when PFSA ionomers have the same side chain length, Π increases with increasing EW due to increased surface activity.⁷ However, in our PFSA monolayers, the lower the EW showed the higher Π_{sat} , which was not consistent with the order of surface activity. It may rely on the formation methods for the PFSA monolayer. For PFSA monolayer, there are two methods; 1) Spontaneous absorption from the bulk onto the air/aqueous dispersion solution interface, Gibbs monolayer,^{8,9} and 2) irreversible adsorption onto the air/water interface by the direct spreading of dispersion, Langmuir monolayer.^{10–13} For the former, the Π significantly correlated with the surface activity, which increases as the EW of the PFSA ionomer increases.⁷ In contrast, for the latter, total amounts of the sulfonic acid group on the interface may be a more important factor for the corresponding Π because Π of the PFSA monolayer originates from the repulsive interaction between sulfonic acid side chains.⁷ The charge densities of EW1100 and EW1000 are 1.60×10^{-19} C nm⁻² and 2.23×10^{-19} C nm⁻², respectively, which means EW1000 has much more repulsive interaction on the saturated interfacial area, resulting in high surface pressure.

Discussion S3. Interfacial behavior of PFSA monolayer by physical compression

For the closely packed PFSA monolayer on the air/water interface, ionomers absorbed on the interface were compressed by physical barriers with a speed of 5 mm min⁻¹ (**Figure S2a**). As shown in **Figure S3b**, for each ionomer, Π gradually increases as ionomer molecules condense and form the packing structure.¹⁴ As PFSA monolayer formed closely packed structure, each PFSA monolayer exhibited a maximum compressional modulus ($C_{s, max}^{-1}$) of 152.43 mN m⁻¹ for EW1100 and 150.31 mN m⁻¹ for EW1000, respectively (**Figure S4**). However, the trough area (*A*) forming the closed packed structure was slightly larger for EW1000 than that for EW1100 because of higher charge density ($A = 234.32 \text{ cm}^2$ for EW1100 and 234.74 cm² for EW1000) (**Figure S3b** and **Figure S4**). Upon further compression, the slope of isotherm, $-d\Pi/dA$, which is the change of Π according to decreasing the trough area, remarkably decreased above certain surface pressure, $\Pi \sim 54 \text{ mN m}^{-1}$, showing the collapse of PFSA monolayer (**Figure S3b**).¹⁵ The PFSA monolayer thus is compressed until $\Pi \sim 54 \text{ mN m}^{-1}$ to make the densely packed and well-aligned structure.



Figure S4. Compression modulus (C_s^{-1}) of PFSA ionomers. C_s^{-1} was calculated by $C_s^{-1} = -A(\partial \Pi/\partial A)_T$ from the isotherm of each PFSA during the compression (A is the trough area.). Maximum compression modulus $(C_{s, \max}^{-1})$ of each PFSA monolayer is 152.43 mN m⁻¹ for EW1100 and 150.31 mN m⁻¹ for EW1000, respectively.

Discussion S4. Langmuir-Blodgett deposition for ultrathin PFSA ionomer membranes with well-ordered morphology

To prepare the ultrathin PFSA ionomer membranes, the PFSA monolayer floating on the air/HCl aqueous solution interface was deposited by Langmuir-Blodgett (LB) method (**Figure S2b**). The LB method is one of the techniques for the deposition of the monolayer from the air/water interface onto the substrate. The LB deposition is a vertical dipping process, and the monolayer on the interface was transferred onto the substrate in a layer-by-layer (LBL) manner.¹⁶ In this regard, the dipping direction depends on whether the substrate has a hydrophilic or hydrophobic surface; starting from up-stroke for the hydrophilic or down-stroke for the hydrophobic substrate. That is, in the up-stroke, hydrophilic side chains of the PFSA membrane contact with the hydrophilic surface, and conversely, the hydrophobic backbones contact with the hydrophobic surface in the down-stroke. After compression until $\Pi \sim 54$ mN m⁻¹, the PFSA monolayer floating on the interface was then sequentially deposited onto the substrate at a dipping rate of 5 mm min⁻¹. The thickness of the ionomer membrane can be easily controlled by the number of stacked layers, considering that the thickness of one layer is ~1.4 nm. After the deposition steps until the target thickness (**Figure S2b**), the ultrathin PFSA membranes on the substrate were dried at room temperature for at least 16 hours.

First, the octadecyltrichlorosilane (OTS) treated Si wafer was used as the substrate to investigate the morphology of PFSA ionomer membranes. From the down–stroke because of the hydrophobic surface of OTS treated Si wafer, each compressed PFSA monolayer was sequentially deposited onto the surface of the wafer with a dipping rate of 5 mm min⁻¹ (**Figure S2b**). The 36 layers of each PFSA monolayer were deposited on one side of the OTS-treated Si wafer (EW10N36 for EW1000 and EW11N36 for EW1100) for sufficient morphology analysis.

Discussion S5. The detailed method of grazing incidence small angle X-ray scattering (GISAXS) experiments

In order to evaluate the nanomorphology of the ultrathin PFSA membrane prepared by LB method, the GISAXS experiments were carried out at a beamline 9A U-SAXS in Pohang Accelerator Laboratory (PAL). Two-dimensional scattering patterns were collected at a grazing incidence angle (α) of 0.15 ~ 0.16 ° between the critical angles for the substrates and the thin films, and were recorded with a MAR CCD detector at room temperature. The X-ray beam wavelength (λ) was 1.12 Å, and the sample-to-detector distance was 1213.85 mm. The d-spacing values (d) between stacked PFSA membranes were calculated from scattering vectors q ($d = 2\pi/q$).



Figure S5. 2D scattering patterns of PFSA ionomer thin films formed by (a) spin coating and (b) dip coating.



Figure S6. Schematic illustration of (a, b) pre-aligned PFSA ionomer monolayer of each EW at the trough area ($A_{\Pi \sim 54 \text{ mN m}^{-1}}$) when the surface pressure (Π) is reached at $\Pi \sim 54 \text{ mN m}^{-1}$, and (c, d) the *d*-spacing of the layered structure of the monolayer at dried state after LB deposition.

Discussion S6. Morphological anisotropy analysis by Herman's orientation factor and critical azimuthal angle

For the quantification of the degree of morphological anisotropy, we estimated Herman's orientation factor, f, of each ultrathin PFSA ionomer membrane. From the extracted intensity profile along the azimuthal angle (ω) at q_z^* (inset image in **Figure 2d**), f was calculated by **Equation S2**.

$$f = \frac{3 < \cos^2 \omega > -1}{2}.$$
 Equation S2

In general, the average of $\cos^2 \omega$ was evaluated between $\omega = 0$ and $\pi/2$ as shown in **Equation S3**,

$$<\cos^{2}\omega> = \frac{\int_{0}^{\pi/2} I(\omega) \sin \omega \cos^{2}\omega \, d\omega}{\int_{0}^{\pi/2} I(\omega) \sin \omega \, d\omega}.$$
 Equation S3

However, ω was corrected and analyzed from 0° to $\omega \sim 73^{\circ}$ because of the Yoneda peak in the q_y -axis, where the information about the structure for this study is absent.^{19,20} The value of *f* is equal to 0, 1, or -0.5, corresponding to an isotropy system, perfect parallel orientation, and perfectly vertical orientation to the plane of a substrate, respectively. Therefore, the concentrated intensity at a small ω without spreading along the angle means that the scattering domains are almost perfectly aligned in the parallel direction to the substrate. In this regard, ultrathin PFSA ionomer membranes had *f* values closer to 1 (f = 0.95 for EW1000 and f = 0.78 for EW1100) compared to PFSA thin films formed by spin coating and dip coating ($f = 0.46 \sim 0.57$). This means that ultrathin PFSA ionomer membranes derived from the pre-aligned structure have well-ordered morphology than PFSA thin films.

Another analytical method for quantifying the structural anisotropy is critical

azimuthal angle, ω^* . ω^* was calculated using the manner of the previous literature.²¹ The scattering intensity was taken out along ω from the center of the scattering pattern. Then, it was integrated (I_{Ω}) as a function of ω as described in **Equation S4**.

$$I_{\Omega} = \int_{0}^{\Omega} I(\omega) d\omega,$$
 Equation S4

where $I(\omega)$ is the scattering intensity as a function of ω . Then, ω^* is defined as the angle at which the integrated value is half as expressed in **Equation S5**.

$$I_{\Omega}(\omega^*)/I_{\Omega = 90} = 0.5,$$
 Equation S5

where ω^* represents the degree of structural anisotropy. 45, 90, and 0 ° of ω^* correspond to random, perpendicular, and parallel orientation, respectively. The ω^* of each EW is 5.8 for EW1100 and 3.9 for EW1000, respectively. Considering the confined PFSA thin film showed $\omega^* \sim 30 - 40^{\circ}$,²¹ it was therefore confirmed that the ultrathin PFSA membranes prepared by LB deposition of the pre-aligned PFSA monolayers have more highly ordered nanomorphology in the parallel direction to substrate.



Figure S7. 1D intensity profiles of GISAXS along (a) *z*-axis, (b) *y*-axis, and (c) the azimuthal angle of EW11N36 (EW1100). The azimuthal angular profile was extracted at q_z^* along the azimuthal angle.



Figure S8. 1D intensity profiles of GISAXS along the azimuthal angle of EW10N36 (EW1000). The azimuthal angular profile was extracted at q^*_z along the azimuthal angle.

Discussion S7. The detailed method of grazing incidence wide angle X-ray scattering (GIWAXS) experiments

The crystal alignment and crystallinity of the ultrathin PFSA membranes were analyzed by the GIWAXS experiments at a beamline 9A in Pohang Accelerator Laboratory (PAL). Twodimensional scattering patterns were collected at a grazing incidence angle (α) of 0.12 ° and were recorded with a MAR CCD detector at room temperature. The X-ray beam wavelength (λ) was 1.12 Å, and the sample-to-detector distance was 221.33 mm. The *d*-spacing values (*d*) in the crystal were calculated from scattering vectors q ($d = 2\pi/q$).

To calculate the crystallinity of ultrathin PFSA ionomer membranes at *z*- and *y*-axis direction, the 1D intensity profile was extracted along each axis. After baseline subtraction, the profile at the range of q = 0.8 - 1.4 Å⁻¹ was fit using the Gaussian function for deconvolution of amorphous and crystalline peaks. To quantification of crystallinity on each axis, the relative crystallinity ($\chi_{c, i}$) on *i*-axis was calculated using **Equation S6**.^{17,18}

$$\chi_{c,i} = \frac{\int_0^\infty I_{c,i}(q)q^2 dq}{\int_0^\infty [I_{c,i}(q) + I_{a,i}(q)]q^2 dq},$$
 Equation S6

where $I_{c,i}(q)$ and $I_{a,i}(q)$ are the intensities of the crystalline and amorphous peaks on *i*-axis, respectively.

In addition, the total crystallinity ($\chi_{c,t}$) was also evaluated to quantify the overall crystal component inside the membrane matrix regardless of the direction. The integrated 1D intensity profiles of amorphous region and crystalline region were extracted in $q \sim 1.05 - 1.18$ Å⁻¹ and 1.14 - 1.27 Å⁻¹ along the azimuthal angle. From the normalized integral intensity, I(q), which is obtained by **Equation S7**, the $\chi_{c,t}$ was estimated by **Equation S8**.

$$I_{\rm d}(q) \approx \int_0^{\pi/2} I_{\rm d}(\omega)(2\pi q) |\sin \omega| \, d\omega$$
, Equation S7

where $I_d(q)$ is the normalized integral intensities of the crystalline, $I_c(q)$, and amorphous region, $I_a(q)$,

$$\chi_{\rm c,t} = \frac{I_{\rm a}(q)}{I_{\rm a}(q) + I_{\rm c}(q)} \times 100,$$
 Equation S8



Figure S9. 1D intensity profiles of GIWAXS along (a) *z*-axis and (b) *y*-axis, and (c) the crystallinity along each axis of EW11N36 (EW1100). The crystallinity of each axis was calculated by **Equation S6**.



Figure S10. The crystallinity along each axis of EW10N36 (EW1000). The crystallinity of each axis was calculated by **Equation S6**.

Discussion S8. Electrolyte uptake properties of ultrathin PFSA ionomer membranes according to deformed morphology

To study the electrolyte uptake behaviors of the membranes under electrochemical devices operating conditions, the membranes were immersed in 3M H₂SO₄ aqueous solution, which is representative electrolyte for electrochemical devices during at least 24 hours, and morphologies of membranes after swelling were analyzed with GISAXS.

As shown in Figure S11a and Figure S12a, ultrathin PFSA membranes still exhibited the anisotropic scattering pattern as shown in dried state, but the localized intensity in z-axis was shift to lower q value. For annealed membranes above $T_{\rm g}$, scattering pattern were also spreading because of random structure, but observed more clearly compared to those of dried membranes. From the 1D intensity profile analysis, it was confirmed that the overall peaks shifted to lower q value than in the dry condition, indicating larger d-spacing, which means that ion channels expanded by swelling (Figure S11b and Figure S12b). The size of enlarged ion channel was \sim 3.5 nm in both EWs, which still much smaller than that of bulk PFSA membranes (\sim 5 nm). In addition, it was observed that the maximum peak located at higher q value as the annealing temperature increase, which means the small ion channel size. Given that degree of swelling of PFSA membrane is determined by the balance between the water absorption of hydrophilic domain and mechanical strength of hydrophobic domain,²² it was understood that these results are due to the increase in the mechanical strength of the hydrophobic part in the membrane with the increase in crystallinity by annealing. In particular, the deformation of aligned structure of ultrathin PFSA membranes after annealing under above T_g , was more clearly displayed owing to expansion of ion channels by swelling. With the localized ionomer scattering patterns spread along the azimuthal angle, the orientation factors of the structure decreased, indicating that the membrane lost the aligned channel morphology (Figure S11a and S11d for EW1100, Figure S12a and S12d for EW1000).



Figure S11. a) 2D GISAXS scattering patterns of ultrathin PFSA ionomer membrane according to EWs and annealing temperatures after swelling with $3M H_2SO_4$ aqueous solution, 1D intensity profiles along (b) *z*-axis and (c) azimuthal angle, and (d) the orientation factor of EW11N36 (EW1100) under each annealing temperature.



Figure S12. a) 2D GISAXS scattering patterns of ultrathin PFSA ionomer membrane according to EWs and annealing temperatures after swelling with $3M H_2SO_4$ aqueous solution, 1D intensity profiles along (b) *z*-axis and (c) azimuthal angle, and (d) the orientation factor of EW10N36 (EW1000) under each annealing temperature.

Discussion S9. Preparation of ultrathin PFSA ionomer membrane/PC50 composite membranes.

To evaluate the ion transport properties of the membrane, a track-etched polycarbonate membrane with simple cylindrical pores with a diameter of 50 nm (PC50) was used as a supporting membrane. The compressed PFSA monolayers with aligned structure on the air/HCl aqueous solution interface were introduced repeatedly on the PC50 by LB deposition (**Figure S13**). Considering the LB method in this study deposited on both sides of the PC support, 22 layers (total thickness: ~ 30 nm, 11 layers on each side of PC50) were deposited on the PC50 to perfectly cover the pore of PC50 without infiltration into pores (**Figure S14 and S15**). After manufacturing the ultrathin PFSA/PC composite membranes, they were treated at 80, 100, and 130 °C for 3 hours, respectively, except at 160 °C, which is similar to T_g of PC ($T_g \sim 165$ °C) and causes destruction of pore structure of PC50. The final composite membranes were denoted as PCEW11-*x* and PCEW10-*x*, where *x* is the treated temperature.



Figure S13. Schematic images of preparation of ultrathin PFSA/PC50 composite membrane from the compressed PFSA monolayer by LB deposition method.



Figure S14. The SEM images of (a) pristine PC50, (b) PCEW11, and (c) PCEW10 membranes. The 50 nm pores seen in the PC50 disappear as the 22 layers of ultrathin PFSA ionomer monolayers are deposited on the surface of the PC membranes. In addition, despite of the thermal treatment at target temperatures (80, 100, and 130 °C), the ultrathin PFSA ionomer membranes covered the surface of PC membrane without defects. Scale bars are 20 μ m.



Figure S15. The cross-sectional SEM images of (a) PC50, (b) PCEW11, and (c) PCEW10. Regardless of treated temperature and EW, the ultrathin PFSA ionomer membranes completely covered the surface of PC50 without infiltration into the pores. Scale bars are $2 \mu m$.



Figure S16. The concentration change on VO^{2+} ion lean part according to time. The concentration increased by the permeation of VO^{2+} ions across the ultrathin PFSA/PC composite membranes.



Figure S17. Proton conductance (κ) of ultrathin PFSA ionomer membranes.

Discussion S10. Estimation of the intrinsic material properties of ultrathin PFSA ionomer membranes

From the *p* and *R*, which are dependent on thickness (*L*) of membranes, we can obtain the intrinsic material properties, VO²⁺ ion permeability (*P*) and proton conductivity (σ), which are not rely on the membrane thickness. Given that ultrathin PFSA membranes are composed of stacked PFSA monolayers, the *P* and σ of ultrathin PFSA membranes can be obtained by a series model of multilayer.⁶ It was confirmed that the *P* of ultrathin PFSA membrane was about 3~4 orders of magnitude lower than that of the commercial membrane, and the membrane annealed at 100 °C showed the lowest permeability with *P*_{EW1100} ~ 2.81 × 10⁻¹⁷ m² s⁻¹ and *P*_{EW1000} ~ 2.19 × 10⁻¹⁶ m² s⁻¹. In proton conductivity, ultrathin PFSA membranes showed 1~2 orders of magnitude lower than that of commercial membranes, and the membrane annealed at 100 °C also exhibited the lowest proton conductivity with $\sigma_{EW1100} \sim 45.91$ mS m⁻¹ and σ_{EW1000} ~ 43.16 mS m⁻¹. From these intrinsic properties, ion-selectivity (*S*) can be obtained by S = σ/P . As a result, *S* of ultrathin PFSA membrane showed higher ion selectivity than that of commercial PFSA membrane. In addition, EW1100 annealed at 100 °C had the highest ion selectivity, showing ~ 800 times higher selectivity than that of the commercial one.

Membrane ^{a)}	Thickness [µm] ^{b)}	Permeability [m ² s ⁻¹] ^{c)}	Conductivity $[mS m^{-1}]^{d}$	S/S _{bulk} ^{e)}
N211	29	5.18×10^{-13}	1082.08 ± 2.42	-
PC50	10	1.30×10^{-12}	389.15 ± 0.86	0.14
PCEW11-RT	10.0383	1.42×10^{-14}	381.05 ± 0.67	12.88
PCEW11-80	10.0377	1.97×10^{-14}	379.38 ± 0.38	9.22
PCEW11-100	10.0365	$7.68 imes 10^{-15}$	378.84 ± 0.53	23.61
PCEW11-130	10.0364	1.62×10^{-13}	385.00 ± 1.86	1.14
PCEW10-RT	10.0380	8.33×10^{-14}	380.58 ± 0.99	2.19
PCEW10-80	10.0362	1.47×10^{-13}	379.32 ± 0.84	1.24
PCEW10-100	10.0361	5.82×10^{-14}	378.19 ± 0.94	3.11
PCEW10-130	10.0317	2.37×10^{-13}	383.91 ± 0.77	0.77
EW11-N1-RT	$1.740 imes 10^{-3}$	$5.46 imes 10^{-17}$	59.43 ± 4.21	521.13
EW11-N1-80	$1.713 imes 10^{-3}$	7.51×10^{-17}	49.54 ± 1.75	315.88
EW11-N1-100	$1.658 imes10^{-3}$	2.81×10^{-17}	45.91 ± 2.22	782.92
EW11-N1-130	$1.653 imes 10^{-3}$	$6.71 imes 10^{-16}$	105.62 ± 29.51	75.31
EW10-N1-RT	1.729×10^{-3}	3.37×10^{-16}	56.42 ± 5.17	80.13
EW10-N1-80	$1.647 imes 10^{-3}$	5.97×10^{-16}	47.77 ± 3.43	38.30
EW10-N1-100	1.641×10^{-3}	2.19×10^{-16}	43.16 ± 3.41	94.29
EW10-N1-130	1.439×10^{-3}	9.16×10^{-16}	78.81 ± 8.07	38.58

Table S1. Intrinsic material properties of membranes

^{a)}EW-N1 means monolayer (PFSA-N1) of each EW stacked on the PC50. ^{b)}The thickness of commercial N211 and PC50 was measured by digital micrometer after fully swelled by 3M H₂SO₄. The thickness of PFSA-N1 of each EW was estimated by half of the *d*-spacing from the GISAXS data of swelled PFSA film (**Discussion S8**). The thickness of PFSA/PC composite membranes was estimated by thickness of stacked 22 layers of PFSA-N1 and PC50. ^{c)}The permeability (*P*) was calculated by **Equation 1**; ^{d)}The proton conductivity (σ) of the membrane was obtained by **Equation 5**. ^{e)}The relative ion selectivity was calculated by *S* of each membrane and bulk Nafion membrane based on the **Equation 6**.



Figure S18. (a) Coulombic efficiency (CE), (b) voltage efficiency (VE), (c) energy efficiency (EE), and discharge capacity of the PCEW11 membranes (EW1100) during the rate performance tests of the VRFBs at various current densities between 40 and 200 mA cm⁻².



Figure S19. (a) Coulombic efficiency (CE), (b) voltage efficiency (VE), (c) energy efficiency (EE), and discharge capacity of the PCEW10 membranes (EW1000) during the rate performance tests of the VRFBs at various current densities between 40 and 200 mA cm⁻².



Figure S20. The SEM images of (a, b) PCEW11-100 and (c, d) PCEW10-100 before and after cell tests. The ultrathin PFSA ionomer membranes exhibited chemical and mechanical stability without defects on the surface despite repeated cell tests at various current densities. Scale bars are $200 \,\mu m$.



Figure S21. (a) efficiencies and (b) change of the discharge capacity of N211 and PCEW10-100 during the long-term cycling performance at 200 mA cm⁻². The VRFB cell with PCEW10-100 showed stably performance comparable with N211 without fluctuation of efficiencies during 500 cycles indicating the structural integrity and durability of ultrathin PFSA membrane.

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