

Electronic Supplementary Information:

Continuous Channels Created by Self-Assembly of Ionic Cross-Linked Polysiloxane/Nafion Nanocomposites

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Experimental Section

Preparation of poly(vinylimidazole)-functionalized polysiloxane/Nafion hybrids

Telomerization of poly(1-vinylimidazole), was carried out by dissolving 4.7 g (50 mmol) of 1-vinylimidazole (Alfa Aesar) and 0.98 g (5 mmol) of 3-mercaptopropyltrimethoxysilane (MPTMS, Dow Corning Corporation) in distilled methanol, followed by the addition of 0.1 g of azobisisobutyronitrile (AIBN, SHOWA). The solution was stirred at the reflux temperature for 12 h in an N₂ gas atmosphere. After reaction completion, the solution was concentrated in vacuo. White precipitates formed upon the addition of diethyl ether to the residue solution at -20 °C. The precipitates were filtrated and washed thoroughly with diethyl ether and dried in vacuo. A yellowish viscous liquid product was obtained with a yield of 67%. Different degree of polymerization was accomplished by using 23.5 g (250 mmol) of 1-vinylimidazole, 0.98 g (5 mmol) of MPTMS, and 0.49 g of AIBN. The average degree of polymerization (*n*) was determined by ¹H NMR spectroscopy, and found to be 6 and 33. The degrees of polymerization

were reproducible in different batch of reaction.

The polymer obtained was further reacted with neat MPTMS (in which the molar ratio of total MPTMS to imidazole group is 10) in 50 ml ethanol solution by hydrolysis of $\text{Si}(\text{OCH}_3)_3$ groups under acidic condition with HCl as catalyst. The molar ratio between the reagents was $\text{HCl}:\text{H}_2\text{O}:\text{Si} = 0.04:3:1$. This solution was then blended with 20% Nafion DE-2020 dispersion followed by casting and slowly removing the solvent from 30 to 150°C to form a composite thin film. The obtained membranes were brown and transparent with a thickness of 140µm. The poly(vinylimidazole)-functionalized silanes with $n = 6$ and 33 were mixed with Nafion DE-2020 dispersion (imidazole/ $\text{SO}_3\text{H} = 0.1$), which were denoted as $\text{M}(\text{VI})_6$ and $\text{M}(\text{VI})_{33}$ membranes, respectively. A control membrane, denoted as $\text{M}(\text{VI})_m$, was prepared by blending neat MPTMS, 1-vinylimidazole monomer (without polymerization) and Nafion DE-2020 (DuPont Fluoroproducts) in a similar fashion. The $\text{M}(\text{VI})_6$ and $\text{M}(\text{VI})_{33}$ membranes were further treated in a 10 wt% H_2O_2 solution for 1 h at 60 °C in order to convert thiol to sulfonate. These H_2O_2 -treated membranes were denoted as s- $\text{M}(\text{VI})_6$ and s- $\text{M}(\text{VI})_{33}$ membranes.

Characterization

The cross-section morphology of the membranes was characterized by transmission electron microscopy (TEM) using a JEOL JEM-1200CX-II microscope operating at 120 kV. The hybrid membranes were then immersed in 1N $\text{Pb}(\text{CH}_3\text{COO})_2$ aqueous solution overnight and rinsed

with water for staining the hydrophilic domains. Subsequently, a 3×5 mm strip was cut from the membranes and dried under vacuum at 80°C for 12 h, and sectioned to yield 50 nm slices using an ultramicrotome. Finally, the slices were picked up with 200-mesh copper grids for TEM observation.

¹H MAS NMR was recorded with a Bruker AVANCE 400 spectrometer, equipped with a 7 mm double resonance probe, operating at 400.13 MHz for ¹H. Typical NMR experimental conditions were as follows: $\pi/2$ duration, 4 μ s; recycle delay, 10 s; spinning speed, 5 kHz.

The ion exchange capacity (IEC) was measured by classic titration.²³ The membranes were soaked in a saturated NaCl solution, with released protons titrated using a 0.05 N NaOH aqueous solution. For better accuracy, each sample was measured three times. The reported IEC values are based on averaged results.

Methanol uptake was measured after immersing the membranes in a pure methanol solution for 12 h and then wiped off the liquid on the membrane surface.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a VG Scientific ESCALAB 210 electron spectrometer using MgK α radiation under a vacuum of 2×10^{-8} Pa. Narrow scan photoelectron spectra were recorded for the N 1s. To compensate for charging effects, binding energies were corrected for covalent C1s at 284.6 eV after curve fitting.

Two types of water in the membranes, freezing and nonfreezing water (bound water), were detected by melting transitions in DSC measurements using a DuPont TA2010 differential scanning calorimeter with a low-temperature measuring head and a liquid nitrogen-cooled heating element. The samples were first cooled from +25 to -50 °C, and then heated at a rate of 5 °C min⁻¹ up to +40 °C. Calculation of the amount of bulk water in the samples was done by integrating the peak area of the melt endotherm. The degree of crystallinity of the water, obtained from the heat of fusion of pure ice, 334 J g⁻¹, was used as a standard, while an empty aluminum pan was used as a reference. The weight fraction of free water (ω_f) to the fully-hydrated membranes can be estimated from the total melting enthalpy (ΔH_m) that is obtained by integration of the transition heat capacity (ΔC_p) over the broad melting temperature interval. The formula of the weight fraction of free water (ω_f) calculation is displayed in the followed equation:

$$\omega_f = \frac{\Delta H_m}{Q_{\text{melting}}} = \frac{\int \Delta C_p dT}{Q_{\text{melting}}}$$

where Q_{melting} is the heat of fusion of bulk ice (334 J/g). The weight fraction of bound water (ω_b) is calculated by subtracting the amount of freezing water (ω_f) from the total water uptake (ω_t). The bound water degree ($\chi = \omega_b / \omega_t$) is further calculated from the ratio of the amount of bound water to the total water uptake.

Proton conductivity of the polymer membranes was measured by an AC impedance

technique using an electrochemical impedance analyzer (CH Instrument model 604A), where the AC frequency was scanned from 100 kHz to 10 Hz at a voltage amplitude of 10 mV. Fully hydrated membranes were sandwiched into a Teflon conductivity cell equipped with Au plates. The temperature dependence of proton conductivity was carried out by controlling the temperature from 30 to 95 °C at a relative humidity of 95 %.

Methanol permeability of membranes was measured at 30°C using a liquid permeation cell composed of two compartments, which were separated by a vertical membrane. The membrane was first immersed in water for 12 h to obtain the well-soaked sample and then set into the measurement cell (the effective area (A): 7.07 cm²). One compartment of the cell ($V_1 = 200$ ml) was filled with a mixed solution of 2M methanol aqueous solution, while the other ($V_2 = 200$ ml) was filled with de-ionized water. The compartments were stirred continuously during the permeability measurement. The methanol concentrations of the compartments, C_2 , were analyzed by a gas chromatograph (VARIAN, 5200GC) equipped with a 3-m capillary column packed with Polarpack Q (poly(ethylene glycol)-1000 supported on Shimalite F). The methanol permeability, P , was then determined by the following equation:

$$P = \frac{1}{AC_1} \frac{C_2(t)}{(t-t_0)} V_2 l$$

where $C_2(t)$ is the methanol molar concentration permeated into compartment B at time t , t is the measuring time, and C_1 denotes the methanol concentration of compartment A. A and l are

the area and thickness of the swollen membrane, respectively.

Oxidative stability was examined by evaluating the weight change before and after immersing the membrane samples in a Fenton's reagent (3% H₂O₂ aqueous solution containing 2 ppm FeSO₄) at 80 °C for 1 h.

Single DMFC test was evaluated using a unit cell with an active area of 5 cm² fed with a 2.0 M methanol aqueous solution at the anode with a rate of 2 ml min⁻¹ by a peristaltic micropump, and oxygen at the cathode with a rate of 100 ml min⁻¹. The membrane electrode assemblies for the single cell test were fabricated as follows. Catalyst ink was prepared by mixing catalyst powder (E-TEK 20 % PtRu/XC-72 for anode and E-TEK 20 % Pt/XC-72 for cathode) with water (2 ml for 1 g of electrocatalyst), and then adding isopropanol (20 ml for 1 g of electrocatalyst) to avoid any ignition. 5% Nafion dispersion (DuPont) was added (0.8 g solid Nafion for 1 g of catalyst) to the catalyst slurry. Catalyst coating on gas diffusion layer (50 wt% wet-proofing carbon paper, Toray) with 5 cm² active area was fabricated by brushing Pt/C catalyst ink. The catalyst loadings on the anode and cathode layers were both 2 mg Pt cm⁻². The catalyst-coated GDLs were hot-pressed with the hybrid membrane or Nafion-117 membrane (DuPont) at 140 °C under 30 kg cm⁻² of pressure.

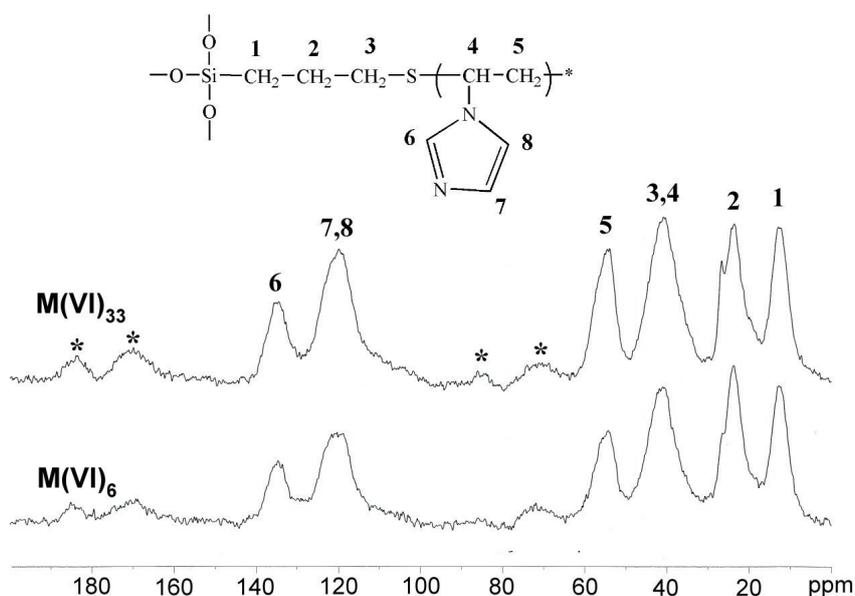


Fig. S1 ^{13}C CP/MAS NMR spectra of the M(VI)_6 and M(VI)_{33} membranes and the corresponding assignment of signals.

^{13}C and ^{29}Si CP/MAS NMR were recorded with a Bruker AVANCE 400 spectrometer, equipped with a 7 mm double resonance probe, operating at 100.6 MHz for ^{13}C . Typical NMR experimental conditions were as follows: $\pi/2$ duration, 4 μs ; recycle delay, 10 s; spinning speed, 5 kHz.

The two peaks at $\delta = 13$ ppm and 24 ppm are ascribed to the methylene carbon in α and β positions of the silicon atom, respectively. The broad peak at 41 ppm is characteristic of sulphide carbon atoms ($-\text{CH}_2-\text{S}-\text{CH}-$), which is composed of two carbon atoms, i.e. **3** and **4** as shown in the inset chemical structure in Fig. S1. The peak at 54 ppm results from the methylene carbon ($-\text{CH}-\text{CH}_2-$) of the poly(vinylimidazole). The other two downfield peaks at $\delta = 120$ ppm and 134 ppm are ascribed to the resonant carbon atoms on the imidazole rings.

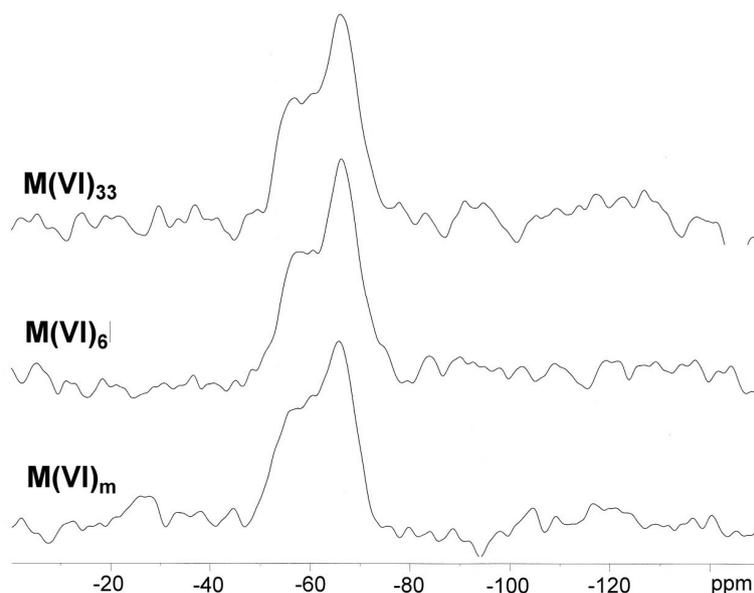


Fig. S2 ^{29}Si CP/MAS NMR spectra of sample M(VI)_m , M(VI)_6 and M(VI)_{33} .

Solid-state ^{29}Si NMR spectroscopy was used to provide information on polysiloxane, such as the various local environments of silicon atoms of the polysiloxane backbone and attaching pendant groups [37]. More specifically, many of the chemical moieties associated with siloxane subunits can be identified by their chemical shifts. The ^{29}Si CP/MAS NMR spectra of samples M(VI)_m , M(VI)_6 and M(VI)_{33} show an intense peak at $\delta = 65$ ppm and a shoulder at $\delta = 56$ ppm, which are attributed to T^3 ($-\text{CH}_2\text{-Si}(\text{O-Si-})_3$) and T^2 resonance ($-\text{CH}_2\text{-Si}(\text{OH})(\text{O-Si-})_2$). In addition, the poly(vinylimidazole) chain has only a minor influence on developing the silicon units; hence, the condensation of the Si-OR and Si-OH groups makes up most of the three-dimensional siloxane network.

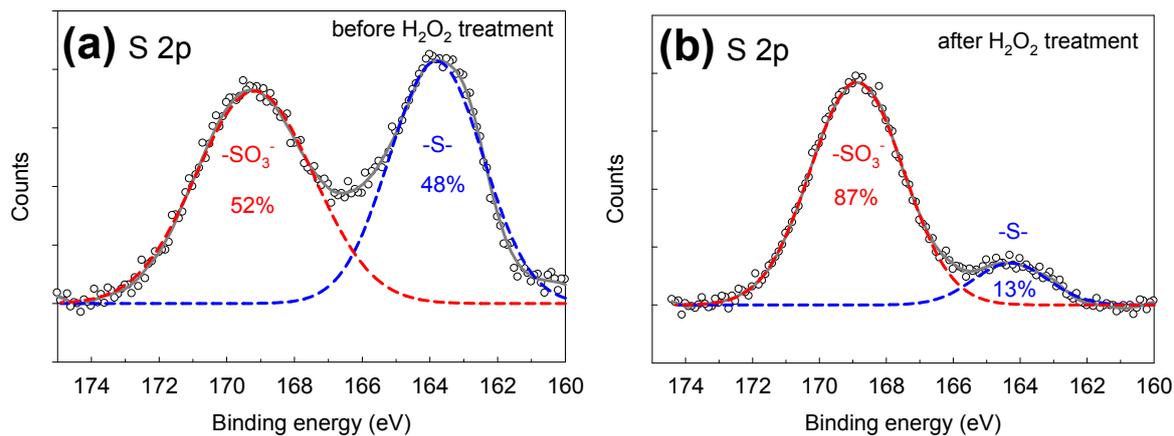


Fig. S3 X-ray photoelectron spectra in the S 2p region of the M(VI)₆ membranes before (a) and after (b) H₂O₂ treatment. (raw data; —, fitted data; ---, deconvoluted data)

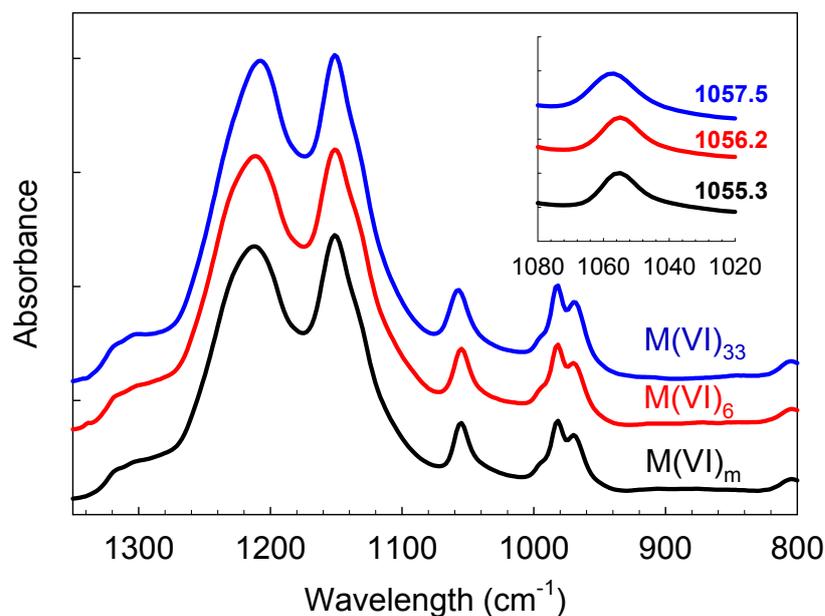


Fig. S4 The ATR/FTIR spectra in the 800-1400 cm⁻¹ region of the M(VI)_m, M(VI)₆ and M(VI)₃₃ membranes.

FT-IR measurements were recorded on a Nicolet 550 system equipped with an attenuated total reflectance (ATR) accessory for the polymer membranes in the range of 4000-600 cm⁻¹. Each sample was vacuum-dried at 80 °C for 24 h to remove the adsorbed water in the sample. The ATR/FTIR spectra in the 800-1400 cm⁻¹ region are shown in Fig. S4. The characteristic absorption bands at 968 and 980 cm⁻¹ are ascribed to the symmetrical stretching of the -COC- groups, while those at 1055 and 1151 cm⁻¹ are respectively assigned to the -SO₃⁻ symmetrical stretching and -CF₂- symmetrical stretching vibrations. The spectra displayed in the inset of Fig. S4 show the -SO₃⁻ symmetrical stretching bands. A progression in the maximum of the symmetrical stretching band toward a higher wave number is observed as the PVI-chain length increases (1055.3 to 1057.5 cm⁻¹). It is known that the shift in the -SO₃⁻ symmetrical stretching peak occurs with a change in the environment of the sulfonic acid groups, i.e. a change in the

radius of the cation, or the ionic interaction between $-\text{SO}_3^-$ and positively-charged functionalities. In the present system, the imidazole ring interacts with the sulfonic acid groups on Nafion, which in turn decreases the frequency of the $-\text{SO}_3^-$ stretching peak. The high wavenumber of the M(VI)₃₃ membrane indicates that the poly(vinylimidazole) chain interacts weakly with $-\text{SO}_3\text{H}$. This could be attributed to the steric effect and/or static repulsion among nearby acid-base pairs.



Fig. S5 The membrane $M(VI)_6$ before (left) and after (right) the oxidative stability test.

Table S1. The IEC value, water content, proton conductivity, and methanol permeability of the composite membranes.

Ionomer	IEC (meq g ⁻¹)	water content, ω_t (wt %) ^a	methanol permeability (cm ² s ⁻¹)	conductivity, σ (S cm ⁻¹) ^b
M(VI) _m	0.85±0.02	16.1±0.2	5.3×10 ⁻⁷	0.128
M(VI) ₆	0.88±0.03	21.9±0.3	3.1×10 ⁻⁷	0.087
M(VI) ₃₃	0.86±0.03	24.5±0.3	3.2×10 ⁻⁷	0.073
s-M(VI) ₆	0.98±0.06	22.8±0.2	6.3×10 ⁻⁷	0.117
s-M(VI) ₃₃	0.96±0.05	25.2±0.5	7.7×10 ⁻⁷	0.122
Nafion-117	0.92	24.3	2.2×10 ⁻⁶	0.071

^a Measured after immersed in water. ^b The proton conductivity at 95°C and 95 % R.H.

As shown in Table S1, increasing the chain length of PVI increases the water content (ω_t , expressed in grams of water adsorbed per gram of hydrated membrane). The low water content of M(VI)_m can be ascribed to the presence of uniformly-distributed vinylimidazoles throughout the membrane. The vinylimidazole monomer lowered the free volume for adsorbed water because of its high affinity to -SO₃H groups.

Table S2. The state of water associated with the channels.

Ionomer	freezing water ω_f (wt %)	bound water ω_b (wt %)	bound water degree, χ (%) ^a	λ_t ^b	λ_b ^c	λ_f ^d
M(VI) _m	3.9	12.2	75.8	12.5	9.5	3.0
M(VI) ₆	3.7	18.2	83.1	17.7	14.7	3.0
M(VI) ₃₃	4.4	20.1	82.0	20.7	16.9	3.8
s-M(VI) ₆	7.9	14.9	65.4	16.7	10.9	5.8
s-M(VI) ₃₃	6.4	18.8	74.6	19.5	14.5	5.0
Nafion-117	9.8	14.5	59.7	19.6	11.7	7.9

^a $\chi = \omega_b/\omega_t$. ^b $\lambda_t = \text{total H}_2\text{O}/-\text{SO}_3\text{H}$. ^c $\lambda_b = \text{bound H}_2\text{O}/-\text{SO}_3\text{H}$. ^d $\lambda_f = \text{free H}_2\text{O}/-\text{SO}_3\text{H}$.

Table S3. Oxidative Stability of the composite membranes and Nafion-117.

Ionomer	Loss, ℓ (wt%)	residue after testing (wt%)
Nafion-117	1.1	98.9
M(VI)_m	1.6	98.4
M(VI)₆	1.8	98.2
M(VI)₃₃	3.7	96.3