Electronic supplementary information:

Sulfonated Nanoplates in Proton Conducting Membranes for Fuel Cells

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Experimental Section

Preparation of Sulfonated α-ZrP nanoplates/Nafion membranes: Typical procedure for preparing the membranes is as follows: α-ZrP was synthesized by the addition of $ZrOCl_2.8H_2O$ to a phosphoric acid solution containng Nafion as stabilizer. The mixture was refluxed for 24 h at 125°C. The gel obtained was then centrifuged, washed with de-ionized water to remove the excess acid, and dried in the oven at 60°C overnight. 1.96 g of 3-mercaptopropyltrimethoxysilane (MPTMS; Dow Corning Corporation) was further reacted with 3.01 g of α-ZrP (in which the ratio of MPTMS to $Zr(HPO_4)_2{\bullet}H_2O$ (Si/Zr ratio) is 1) in 50 ml THF solution by hydrolysis of $Si(OR)_3$ groups under acidic condition with HCl as catalyst ($HCl:H_2O:Si = 0.04:3:1$). 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 membrane obtained was further oxidized in 30% H_2O_2 solution at 60°C for 1 hour. The formation of sulfonic acid on s-ZrP was examined by the S 2p signal in XPS spectra. (Fig. S4a in the Supporting Information). Different amount of s-ZrP nanoplates, which has Si/Zr = 1, were mixed with Nafion DE-2020 dispersion (solid content (s-ZrP/s-ZrP+Nafion soid) = 5%, 10%, 20%, 30%) denoted as **A**, **B**, **C**, and **D** composite membranes, respectively. These membranes were characterized by XPS in the C 1s region (Fig. S4b). Two control membranes, denoted as $C_{2.0}$ and $C_{0.5}$, were prepared with Si/Zr = 2 and 0.5, respectively. The table explaining the amounts of reagents during the preparation is shown in Table S1.

Table S1. The amount of reagents for preparing s-ZrP with different Si/Zr ratios.

Si/Zr ratio of s-ZrP	$Zr(HPO_4)_2 \bullet H_2O$ (g)	MPTMS (g)	HCl (mg)	H_2O (g)
0.5	3.01	0.98	7.3	0.27
1.0	3.01	1.96	14.6	0.54
2.0	1.51	1.96	14.6	0.54

Characterizations: The ion exchange capacity was measured by classical titration. The membranes were soaked in a saturated NaCl solution. Released protons were titrated using a 0.05 N NaOH aqueous solution. XRD was carried out in a Rigaku RINT2100 X-ray diffractometer with Cu-K_α radiation (λ=0.1542 nm) operated at 40 kV and 40 mA. The morphology of α-ZrP nanoplates and the cross-section morphology of the membranes were observed with a SEM from JEOL equipped with an energy dispersive X-ray spectroscopy (EDX) detector. TEM was carried out on a JEOL JEM-1200CX-II microscope operating at 120 kV.

Proton conductivity of the polymer membranes was measured by an ac impedance technique using an electrochemical impedance analyzer (CH Instrument model 604A). Fully hydrated membranes were sandwiched into a Teflon conductivity cell equipped with Au plates. The measurement of proton conductivity was carried out by controlling the temperature from 30 to 95 °C at relative humidity from 30 to 95%. Oxidative stability was examined by immersing the membrane samples in Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80°C for 1 h.

Single PEMFC test was evaluated using a unit cell with an active area of 5 cm^2 fed with hygrogen at the anode with a rate of 100 mL min^{-1}, and oxygen at the cathode with a rate of 100 mL min^{-1}. The membrane electrode assemblies for the single cell test were fabicated as follows. Catalyst ink was prepared by mixing catalyst powder (E-TEK 20 % Pt/XC-72 for both anode and 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 (GDL, Toray 50 wt% wet-proofing carbon paper) with 5 cm^2 active area was fabricated by brushing Pt/C catalyst ink. The catalyst loadings on the anode and cathode layers were both 0.5 mg Pt cm^{-2}. The catalyst-coated GDLs were hot-pressed with the hybrid membrane or Nafion-117 membrane (Du Pont) at 140 ^{o}C under 30 kg cm^{-2} of pressure. The working temperature of humidifiers was set at 90^{o}C during the test. The current output was collected at cell temperature of 80 and 100 ^{o}C, respectively.

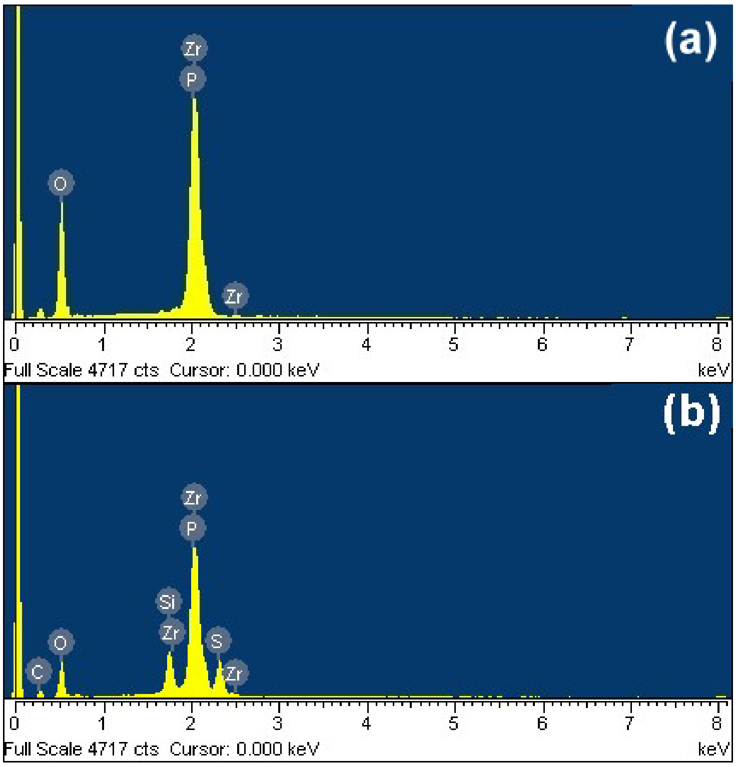

Fig. S1. EDS patterns of (a) α-zirconium phosphate without Nafion and (b) MPTMS-functionalized ZrP nanoplates.

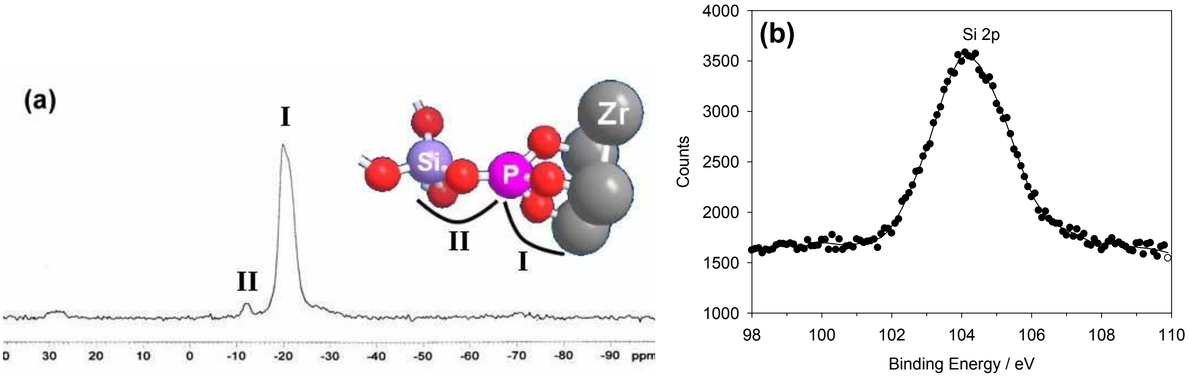

Fig. S2. (a) ^{31}P MAS NMR spectra of s-ZrP/Nafion composite membrane **C.** (b) XPS spectrum in the Si 2p region for the s-ZrP nanoplates.

^{31}P MAS NMR were recorded with a Bruker AVANCE 400 spectrometer, equipped with a 7 mm double resonance probe, operating at 400.13 MHz for ^{1}H and 161.98 MHz for ^{31}P. Typical NMR experimental conditions were as follows: $\pi/2$ duration, 4 μs; recycle delay, 10 s; spinning speed, 10 kHz. Chemical shifts were externally referenced to *ortho*-phosphoric acid at 0.0 ppm.

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

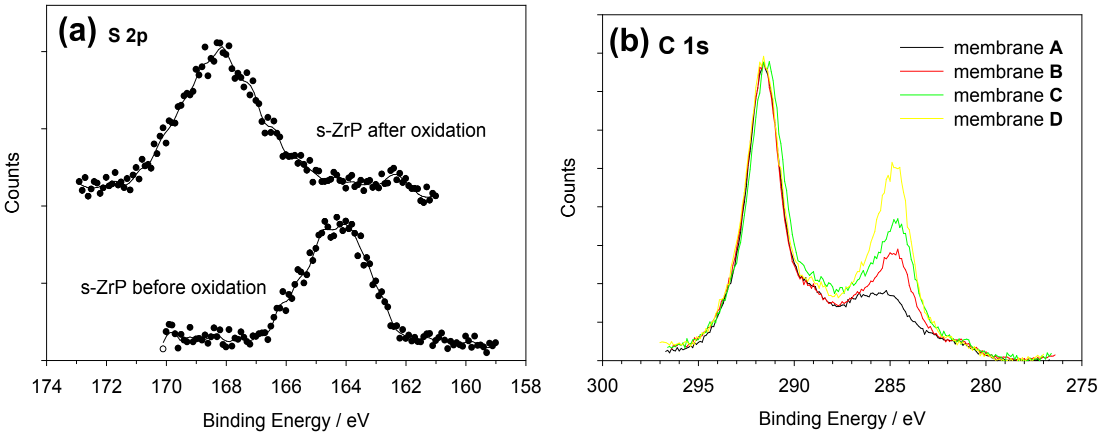

Fig. S3. (a) Comparison of the XPS spectra in the S 2p region for s-ZrP nanoplates before and after oxdative treatment in 30% H_2O_2 solution. (b) XPS spectra in the C 1s region for membranes **A**, **B**, **C** and **D**. All C 1s spectra were normalized to the maximum of 291.6 eV signal.

In Fig. S3a, the S 2p signal of –SH at 164 eV has shifted to 168 eV which referred to sulfonic acid groups. In Fig. S3b, the signal at 291.6 eV is attributed to the fluorinated carbon of Nafion. The presense of the component at 284.6 eV, which is attributed to the C—H groups, indicates the MPTMS-modified ZrP has been successfully blent with Nafion. As s-ZrP content increases, the intensity of C—H peaks increase compared with that of the C—F peak.

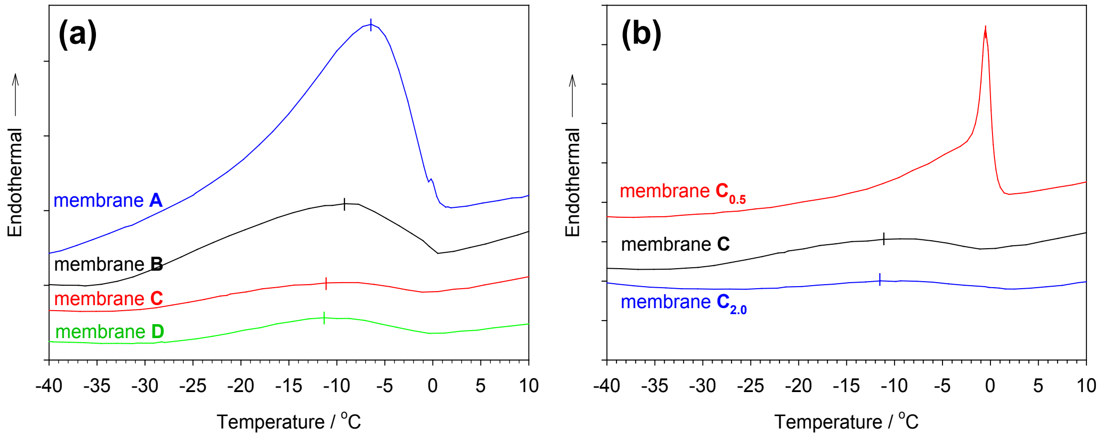

Fig. S4. (a) DSC thermograms indicating the melting of water in the fully hydrated composite membranes with various s-ZrP contents. (b) Comparison among the thermograms of the membranes having 20wt% s-ZrP with Si/Zr ratio of 0.5, 1.0 and 2.0.

Table S2. The state of water in the sulfonated zirconium phosphate nanoplates/Nafion ionomers.

ionomer	T_m (°C)[a]	Water Content, ω_t (wt %)	Freezing Water, ω_f (wt %)	Bound Water, ω_b (wt %)	Bound Water Degree, χ (%)[b]
A	-6.4	21.7	5.0	16.7	77.0
B	-9.2	18.0	3.0	15.0	83.3
C	-11.1	14.0	0.7	13.3	95.0
D	-11.3	13.4	0.9	12.5	93.3
$C_{0.5}$	--	13.2	1.7	11.5	87.1
C_2	-11.5	19.7	0.3	19.4	98.5
Nafion-117	-3.4	24.5	10.1	14.4	58.8

[a] Melting point of water.

[b] $\chi = \omega_b/\omega_t$

Two types of water, freezing and nonfreezing water (bound water), in the membranes 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 with 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 Jg^{-1}, was used as a standard. 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:

$$\omega_{\mathrm{f}} = \frac{\Delta H_{\mathrm{m}}}{Q_{\mathrm{melting}}} = \frac{\int \Delta C_P dT}{Q_{\mathrm{melting}}}$$

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.

Table S3. Methanol Permeability and Selectivity of the MPTMS-Functionalized ZrP / Nafion Composite Membranes and the Nafion-117.

Ionomer	Proton Conductivity, σ [wt%][a)]	MeOH permeability, P [cm^2 s^{-1}]	Selectivity ×10^{-4} [S cm^{-1} sec cm^{-2}] [b)]
A	0.028	1.4×10^{-6}	2.0
B	0.039	7.7×10^{-7}	5.1
C	0.050	5.5×10^{-7}	9.1
D	0.033	4.4×10^{-7}	7.5
C$_{0.5}$	0.035	5.0×10^{-7}	7.0
C$_{2.0}$	0.046	4.7×10^{-7}	9.8
Nafion-117	0.026	2.4×10^{-6}	1.1

[a)] 30°C, 95% R.H. [b)] Selectivity = σ/P.

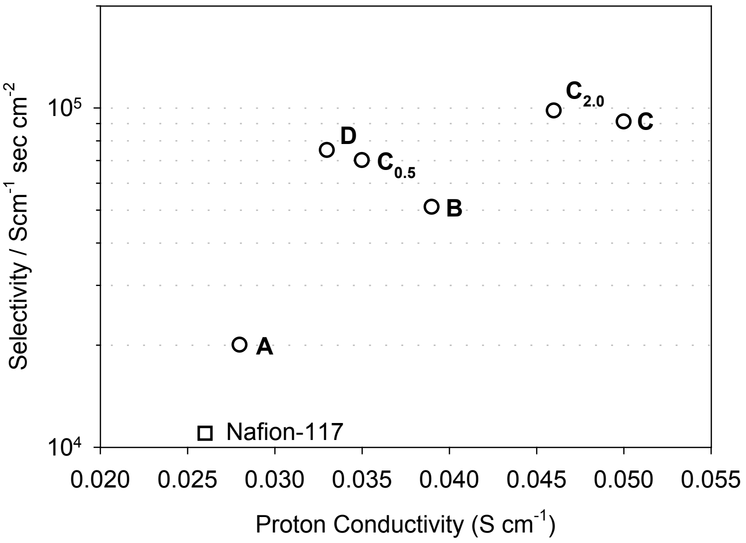

Fig. S5. The performance tradeoff plot of conductivity vs selectivity.

Methanol permeability of the composite membranes was measured using a liquid permeation cell composed of two compartments, which were separated by a vertical membrane. The membrane was first immersed in water to get the well-swollen sample and then set into the measurement cell (the effective area (A): 7.07 cm^2). One compartment of the cell (V_1) 200 mL) was filled with a mixture solution of 2 M methanol aqueous solution. The other (V_2) 200 mL) compartment was filled with deionized water. The compartments were stirred continuously during the permeability measurement at a fixed temperature

30°C. The methanol concentrations of the compartments, C_2, were analyzed on 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 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 measuring time, and C_1 is the methanol concentration of compartment A. A and l are the area and thickness of the swollen membrane, respectively.

Table S3 lists the methanol permeability of composite membranes. The methanol permeability of Nafion-117 is 2.4×10^{-6} cm^2 s^{-1}, which is consistent with the reported value of 2.3×10^{-6} cm^2 s^{-1} at room temperature. The permeabilities of the composite membranes range from 1.1×10^{-6} to 4.4×10^{-7} cm^2 s^{-1}. The lowest permeability obtained is 4.4×10^{-7} cm^2 s^{-1} for membrane **D**. The performance trade-off between permeability and conductivity is shown in Fig. S5. The membrane **C** is about 8.3 times more slective than Nafion-117. When decrease the concentration of surface sulfonic acid groups on ZrP (membrane $\mathbf{C_{0.5}}$), the selectivity decreases about 23%, mainly because of decreae in conductivity. As for memabrane $\mathbf{C_{2.0}}$, the selectivity increases slightly. For Nafion-based membranes, methanol transport mainly occurs through the ion-cluster pores and the connecting ion channels. In the present study, the surface sulfonic acid groups with higher density on ZrP absorb free water and build up a much denser water layer, as evidenced in the DSC analysis. Therefore, the good methanol barrier-property of s-ZrP/Nafion composite membranes can be ascribed to the bound water layer and the intrinsic lamella structure of ZrP.

Table S4. Electrode Kinetic Parameters of s-ZrP /Nafion composite membrane **C** and Nafion-117.

Ionomer	Cell Temperature (°C)	E_0 (mV)	b (mV dec^{-1})	R (ohm cm^2)	Power Density (mW cm^{-2})
C	80	1004	71.5	0.178	322
	100	1001	62.0	0.040	541
Nafion-117	80	994	53.8	0.287	274
	100	992	72.7	0.079	454

[a] 30°C, 95% R.H. [b] Selectivity = σ/P.

For the performance evaluation of the PEMFC, the cell was allowed to run at 80 and 100 °C with the anode and cathode humidifier at 80 °C. The cell potential (E) versus current density (i) data were analyzed by fitting the PEMFC data points to 0-D model expression:

$$E = E_0 - b \cdot \log(i) - R \cdot i$$

where E and i are the measured cell potential and current density. E_0 is the open circuit potential, b is the Tafel slope, related to the electrode performance when the rate-limiting step is the electrolytic reaction, and R accounts for the linear variation of overpotential with current density primarily due to ohmic resistance.

The Tafel slopes of Nafion-117 for the activation region increases from 53.8 to 72.7 mV dec^{-1} when the cell temperature elevates from 80 to 100 °C. This can be ascribed to the poor membrane/electrode interfacial assembly due to membrane dehydration. For membrane C, a comparatively higher Tafel slope (71.5 mV dec^{-1}) than Nafion-117 is obtained at 80°C, which is likely due to the interfacial compromise. This indicates that Nafion-117 has better compatibility at 80°C to the electrode than membrane C. In catalytic layers, low molecular weight Nafion is used as a binder to cohere the Pt/C catalysts together. Thus, the nature of electrode is much close to Nafion-117, which enables a good adhesion between electrodes and the Nafion-117. When the cell temperature increases to 100 °C, the Tafel slope of membrane C reduces to 62.0 mV dec^{-1}.

This indicates that the membrane/electrode interfacial assembly is not deteriorated by the elevated temperature, but instead the fast kinetic help the activation of catalysts.