Crystalline Polyoxometalate (POM)-Polyethylene Glycol (PEG) Composites aimed as Non-Humidified Intermediate-Temperature Proton Conductors

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KEYWORDS

Polyoxometalates, Polyethylene glycol, Proton conduction, Crystal structures

ABSTRACT

Crystalline polyoxometalate (POM)-polyethylene glycol (PEG) composites aimed as non-humidified intermediate-temperature proton conductors were synthesized and characterized by single crystal and powder XRD, solid state MASNMR, and TG-DTA measurements. Among the POM-PEG composites, $\text{Cs}_{2.7}\text{H}_{0.3}[\text{PW}_{12}\text{O}_{40}] \cdot 1.2\text{PEG}1000$ (**CsHPW-PEG1000**) possessed one-dimensional channels with diameters of ca. 6 and 8 Å, where PEG probably resided, and showed the best performance as a proton conductor ($1.2 \times 10^{-5} \text{ S cm}^{-1}$ at 443 K). Proton conductivities

of POM-PEG composites decreased by the increase in molecular weights of PEG (**CsHPW-PEG12000**) or anion charges (**CsHSiW-PEG1000**). Variable contact time ^{13}C -CP (cross polarization) MASNMR revealed that local mobility (i.e., segmental motion) of PEG is related to the trends in proton conductivities. These results show that amount of acidic protons (H^+) is not the primary factor in proton conduction and that segmental motion of PEG assists the proton hopping among POMs in the crystal lattice of POM-PEG composites.

1. Introduction

Proton conduction is important for the performance of solid electrolytes in fuel cells. It is well known that sulfonated fluorocarbon polymers (Nafion) exhibit high proton conductivity and chemical stability under humidified conditions at room temperature [1,2]. Operation of proton conductors at intermediate temperatures (373–523 K) is important especially in terms of reaction kinetics and carbon monoxide poisoning of the electrodes [3]. However, Nafion has a limitation to its use because of dehydration and glass transition [1,4]. In this temperature region, anhydrous oxo-acid salts such as CsHSO_4 [5,6] and CsH_2PO_3 [7] are able to conduct protons via hopping among the oxo-anions. Recently, non-humidified intermediate-temperature proton conduction of metal-organic frameworks (MOFs) loaded with protic organic guests have received great attention. For example, composites of $\text{Al}(\text{OH})(1,4\text{-naphthalenedicarboxylate})$ [8] and $\text{Na}_3(2,4,6\text{-trihydroxy-1,3,5-benzenetrisulfonate})$ [9] showed proton conductivities of $2.2 \times 10^{-5} \text{ S cm}^{-1}$ (393 K) and $5.0 \times 10^{-4} \text{ S cm}^{-1}$ (423 K), respectively.

Polyoxometalates (POMs) are nano-sized anionic metal-oxygen clusters of early transition metals and have stimulated research in broad fields of science [10-12]. The negative charges of POMs are smeared homogeneously over the external surface oxygens so that effective surface charge densities of POMs are small. Therefore, POMs are suitable as counter anions for proton

conduction, and it is well known that Keggin-type heteropolyacids ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$) exhibit high proton conductivity under humidified conditions at room temperature [13]. However, application of heteropolyacids is limited by the extreme sensitivity of conductivity to the relative humidity (RH) and temperature [14]. On the other hand, polyethylene glycol (PEG) has been widely studied as polymer electrolytes [15]. PEG can solvate inorganic salts, and it is known that segmental motion of the polymer chain assists cation transport especially at high temperatures [15].

Based on these considerations, we reached an idea to synthesize non-humidified intermediate-temperature proton conductors by the combination of POMs with polymers. There are only a few studies dealing on composites of POMs with polymers and their proton conduction. For example, Bourlinos *et al.* synthesized a liquid composite with $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and PEG-containing quaternary ammonium cation, exhibiting a proton conductivity of $6 \times 10^{-4} \text{ S cm}^{-1}$ at 413 K under a non-humidified condition [16]. Lakshminarayana *et al.* synthesized a series of hybrid membranes of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ or $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ with organosilanes, exhibiting proton conductivity of $10^{-2} \text{ S cm}^{-1}$ at 363 K and 90% RH [17]. Tong *et al.* prepared hybrids of $\text{H}_6\text{PV}_3\text{W}_9\text{O}_{40}$ and PEG or polyvinylpyrrolidone (PVP) exhibiting proton conductivity of 10^{-3} – $10^{-2} \text{ S cm}^{-1}$ at room temperature and 75% RH, and reported that the activation energies of proton conduction lowered by the hybridization [18]. However, the reported composites [16-18] are liquids or amorphous and can operate only under relatively low temperatures and/or high humidity environments. Moreover, crystalline composites may provide a better understanding of the composition-structure-function relationship. In this work, a series of crystalline POM-PEG composites aimed as non-humidified intermediate-temperature proton conductors were synthesized.

2. Experimental

2.1 Material and measurements

$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ [19] and $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ [20] were synthesized according to previously reported methods. CsNO_3 and polyethylene glycol were purchased from Kanto Kagaku and used as received. The composites will be denoted as **CsHPW-PEG m** or **CsHSiW-PEG m** hereafter, by the type of counter cation (Cs^+), POM ($[\text{PW}_{12}\text{O}_{40}]^{3-}$ or $[\text{SiW}_{12}\text{O}_{40}]^{4-}$), and average molecular weight of PEG (m).

Combustion analysis (Elementar, vario MICRO cube) was used for the quantitative analysis of C, H, and N. Inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent Technologies, ICP-OES720) was used for the quantitative analysis of the inorganic elements. Atomic absorption spectroscopy (AAS) analysis (Hitachi, ZA3000) was used for the quantitative analysis of alkali metals. Thermogravimetry-differential thermal analysis (TG-DTA) data were measured with a Thermo Plus 2 thermogravimetric analyzer (Rigaku Corporation) with $\alpha\text{-Al}_2\text{O}_3$ as a reference under a dry N_2 flow (100 mL min^{-1}) in the temperature range of 293–773 K with an increasing rate of 5 K min^{-1} . Powder X-ray diffraction (XRD) patterns were measured with a New advance D8 X-ray diffractometer (Bruker) by using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$, 40 kV-40 mA) at $2\theta = 3\text{--}40 \text{ deg}$ and 1.8 deg min^{-1} . Solid state magic angle spinning (MAS) NMR spectra were recorded with an AVANCE 400WB spectrometer (Bruker) and the resonance frequencies were 100.6 MHz and 400.2 MHz for ^{13}C and ^1H , respectively. MAS rates were 5 and 10 kHz for ^{13}C and ^1H , respectively, and adamantane (^1H : 1.91 ppm, ^{13}C : 28.8 and 38.3 ppm) was used as an external standard for the calibration of chemical shifts. Single pulse excitation with proton decoupling (Figures 2a and 6a) or cross polarization with contact times of 0.025–2.0 ms (Figure 7) were used for the ^{13}C -MASNMR measurements. Alternating current (AC)

impedance measurements: About 0.1 g of the compounds were compressed at 100 kgf cm⁻² into pellets of 10 mm in diameter and ca. 0.5 mm in thickness. AC impedance measurements were carried out in a heat chamber at 403–443 K with a BioLogic VMP3 multi-channel Potentiostat/Galvanostat (Science Instruments) over the frequency range of 5 Hz to 500 kHz and AC amplitudes of 50 or 100 mV. Gold electrodes were attached on both faces of the pellets. Bulk conductivities were estimated by semicircle fitting of Nyquist plots.

2.2 Synthesis

A typical method to synthesize POM-PEG composite is as follows: Into a Teflon lined hydrothermal autoclave reactor (23 mL), 0.50 g of H₃PW₁₂O₄₀·*n*H₂O (0.17 mmol), 7.0 g of PEG1000 (average molecular weight *m* = 1000) dissolved into 7.0 mL of H₂O (volume of H₂O was changed to 12.0 mL for PEG12000), and 0.10 g of CsNO₃ (0.51 mmol) were added. The reactor was heated at 373 K for 12 h and cooled over 36 h to room temperature. Colorless crystals were obtained in 50–70% yield. Synthetic methods were basically the same when H₄SiW₁₂O₄₀·*n*H₂O was used instead of H₃PW₁₂O₄₀·*n*H₂O. Characteristic bands of POM and PEG were observed in the IR spectra of POM-PEG composites (Figure S1).

Elemental analysis of **CsHPW-PEG1000** (Cs_{2.7}H_{0.3}[PW₁₂O₄₀]·1.2PEG1000): C 14.68 (14.59), H 2.40 (2.48), Cs 8.02 (8.08), P 0.70 (0.70), W 49.42 (49.66). Elemental analysis of **CsHPW-PEG12000** (Cs_{2.6}H_{0.4}[PW₁₂O₄₀]·0.10PEG12000): C 14.84 (14.83), H 2.55 (2.53), Cs 7.73 (7.76), P 0.70 (0.70), W 48.40 (49.56). Elemental analysis of **CsHSiW-PEG1000** (Cs_{2.9}H_{1.1}[SiW₁₂O₄₀]·1.6PEG1000): C 17.74 (17.77), H 2.94 (3.03), Cs 7.84 (7.93), Si 0.57 (0.58), W 45.00 (45.37).

2.3 Single crystal X-ray diffraction (XRD)

X-ray diffraction data of **CsHPW-PEG1000** and **CsHSiW-PEG1000** were collected at 93 K with a CCD 2-D detector by using Rigaku Saturn diffractometer with graphite monochromated Mo K α radiation. Structures were solved by direct method, expanded using Fourier techniques, and refined by full-matrix least-squares against F^2 with the SHELXL package. Cesium, phosphorus, silicon, and tungsten atoms were refined anisotropically, while oxygen atoms were refined isotropically. Positions of PEG atoms could not be resolved. While the lengths of a and b axes in **CsHSiW-PEG1000** were 27.823(7) and 27.836(7) Å, respectively, and similar, the structure did not converge with a tetragonal cell. See Table 1 for the crystallographic parameters. CCDC 1051215 and 1051217 contain the crystallographic data for **CsHPW-PEG1000** and **CsHSiW-PEG1000**, respectively.

3. Results and discussion

3. 1. Crystal structure and characterizations of **CsHPW-PEG1000**

Figure 1a shows the crystal structure of **CsHPW-PEG1000** in the ab -plane. POMs were packed in a monoclinic cell, and the negative charges of POM (-3) were neutralized by Cs $^+$. Elemental analysis showed that the Cs $^+$ to POM ratio in **CsHPW-PEG1000** was 2.7 : 1, suggesting that 0.3 mol mol $^{-1}$ of acidic protons (H $^+$) exist in the crystal lattice. Changes in synthetic conditions (amount of water and POM : CsNO $_3$: PEG1000 ratio) affected the yield but not the amount of cesium in **CsHPW-PEG1000**. Multiple syntheses and elemental analyses of **CsHPW-PEG1000** confirmed that the amounts of cesium in the compounds were 2.70 ± 0.05 .

As shown by the space filling model (Figure 1b), one-dimensional channels with diameters of ca. 6 and 8 Å existed along the c -axis, and Cs $^+$ resided in the larger channel. While positions of PEG atoms could not be resolved by single crystal X-ray diffraction (XRD) due to severe disordering, existence of PEG could be confirmed by ^{13}C -magic angle spinning (MAS) NMR

(Figure 2a): A large signal and a small signal were observed at 70.2 ppm and 61.4 ppm, respectively. The former and latter signals could be reasonably assigned to the methylene and terminal carbons of PEG, respectively [21]. ^1H -MASNMR spectrum showed a signal centered at 3.8 ppm (Figure S2), which agreed with the position of methylene protons of PEG [22]. These results suggest that PEG exists in the one-dimensional channels of **CsHPW-PEG1000**.

Thermogravimetry (TG) of **CsHPW-PEG1000** (Figure 2b) showed no weight loss up to 503 K (230 °C), suggesting that the compound is anhydrous. Hydrophobicity of **CsHPW-PEG1000** was confirmed by a water sorption measurement at 298 K (Figure S3): Amount of water sorption was ca. $4\text{ cm}^3\text{ g}^{-1}$ at $P/P_0 = 0.6$, and was much smaller than that of $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ (ca. $60\text{ cm}^3\text{ g}^{-1}$ at $P/P_0 = 0.6$) [23]. Weight loss of **CsHPW-PEG1000** occurred in one-step between 503–773 K (25.2%), which fairly agreed with the amount of PEG (27.2%) calculated by the results of elemental analysis. Differential thermal analysis (DTA) curve showed an intense sharp endothermic peak at 443 K (170 °C).

3. 2. Effects of molecular weights of PEG

Powder XRD patterns of **CsHPW-PEG m** ($m = 1000$ and 12000) are shown in Figure 3. Experimental pattern of **CsHPW-PEG1000** (Figure 3b) well agreed with that calculated from the single crystal data (Figure 3a), confirming that the crystal structure shown in Figure 1a represented the whole bulk. Experimental pattern of **CsHPW-PEG12000** (Figure 3c) was similar to that of **CsHPW-PEG1000** (Figure 3b), showing that molecular weights of PEG had little effect on the crystal structures of POM-PEG composites. Existence of PEG in **CsHPW-PEG12000** was confirmed by ^{13}C -MASNMR (Figure S4). Notably, POM-PEG composites could not be obtained when PEG with molecular weights of less than 1000 (e.g., PEG600, PEG400) were used.

Powder XRD patterns of **CsHPW-PEG1000** after heating at 423 K and 453 K are shown in Figures 3d and 3e, respectively. The pattern largely changed after heating at 453 K. The pattern at 453 K well agreed with that calculated with the crystal structure of $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ (Figure 3f) [22], suggesting that phase separation into PEG and $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ has occurred. The crystal structure of $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ is non-porous and can be described by a body-centered cubic packing of POMs (Figure S5), which is totally different from that of **CsHPW-PEG1000**. According to these results, it can be concluded that the intense sharp endothermic peak at 443 K in the DTA curve (Figure 2b) corresponds to the melting point of **CsHPW-PEG1000**. Notably, the melting point of PEG1000 is about 313 K [25], so that inclusion of PEG1000 into the crystal lattice has largely improved the heat stability. DTA curve of **CsHPW-PEG12000** (Figure S6) showed an intense sharp endothermic peak at 458 K, showing that the melting point of POM-PEG composites increase with the molecular weights of PEG [26].

Figure 4a shows the Nyquist plots of the impedance spectra of **CsHPW-PEG1000** at 413–443 K ($\text{RH} < 1\%$). Proton conductivity estimated from the spectrum at 413 K was $1.1 \times 10^{-6} \text{ S cm}^{-1}$ and reached up to $1.2 \times 10^{-5} \text{ S cm}^{-1}$ by the temperature increase to 443 K. Activation energy calculated from the proton conductivities as a function of temperature using the Arrhenius equation was 1.3 eV ($1.3 \times 10^2 \text{ kJ mol}^{-1}$) (Figure S7) and quite large, suggesting that protons transport through the crystal lattice via thermal hopping. In fact, proton conductivity of a deuterated compound **CsDPW-PEG1000** was $< 10^{-8} \text{ S cm}^{-1}$ at 443 K, and a large isotope effect was observed [28]. Proton conductivity of **CsHPW-PEG12000** was $< 10^{-8} \text{ S cm}^{-1}$ at 413 K and reached up to $2.1 \times 10^{-7} \text{ S cm}^{-1}$ by the temperature increase to 443 K, but still smaller than **CsHPW-PEG1000** by two orders of magnitude (Figure 4b and Table 2).

3. 3. Effects of anion charges

Next, $[\text{PW}_{12}\text{O}_{40}]^{3-}$ was substituted with $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ to investigate the effect of anion charge. Figure 5a shows the crystal structure of **CsHSiW-PEG1000** in the *ab*-plane. POMs were packed in an orthorhombic cell, and the negative charges of POM (-4) were neutralized by Cs^+ . Elemental analysis showed that the Cs^+ to POM ratio in **CsHSiW-PEG1000** was 2.9 : 1, suggesting that 1.1 mol mol $^{-1}$ of H^+ exist in the crystal lattice. The closest distance between the oxygen atoms of adjacent POMs was 8.6 Å, and considering that the van der Waals radius of oxygen is 1.5 Å [27], the distance between the adjacent POMs is estimated to be larger than 5.6 Å and enough for PEG to reside (see Figure 5b). While positions of PEG atoms could not be resolved by single crystal XRD due to severe disordering, existence of PEG could be confirmed by solid state MASNMR (Figures 6a and S8). TG of **CsHSiW-PEG1000** (Figure 6b) showed no weight loss up to 543 K (270 °C), suggesting that the compound is anhydrous. DTA curve showed an intense sharp endothermic peak at 403 K (130 °C) and 433 K (160 °C). Powder XRD pattern of **CsHSiW-PEG1000** after heating at 413 K (Figure S9) shows that a phase transition occurred at the first endothermic peak (403 K).

Figure 6c shows the Nyquist plots of the impedance spectra of **CsHSiW-PEG1000** at 403 K and 413 K. Proton conductivities estimated from the spectra at 403 K and 413 K were 9.3×10^{-8} S cm $^{-1}$ and 3.0×10^{-7} S cm $^{-1}$, respectively, and smaller than that of **CsHPW-PEG1000** (Table 2). Since the amount of H^+ in **CsHSiW-PEG1000** is 1.1 mol mol $^{-1}$ and larger than that of **CsHPW-PEG1000** (0.3 mol mol $^{-1}$), amount of H^+ is not the primary factor in proton conduction of POM-PEG composites. The increase in anion charge from 3 ($[\text{PW}_{12}\text{O}_{40}]^{3-}$) to 4 ($[\text{SiW}_{12}\text{O}_{40}]^{4-}$) would increase the electrostatic interaction between PEG and the constituent ions, so that the local mobility (i.e., segmental motion) of PEG would have changed.

3. 4. Correlation between local mobility of PEG and proton conductivity

In order to compare the local mobility of PEG among the POM-PEG composites, variable contact time ^{13}C -CP (cross polarization) MASNMR spectroscopy was utilized. This technique provides time constants for magnetization buildup (T_{CH}) and subsequent decay ($T_{1\rho(\text{H})}$) from the following equation,

$$I(t) = I_0 (1 - T_{\text{CH}} / T_{1\rho(\text{H})})^{-1} \{ \exp(-t / T_{1\rho(\text{H})}) - \exp(-t / T_{\text{CH}}) \} \quad (1)$$

where $I(t)$ and I_0 represent the intensity of the signal at contact time t and the theoretical maximum intensity of the signal, respectively [30]. Since T_{CH} depends on both mobility and internuclear distance between ^1H and ^{13}C species, neighboring proton environment (molecular weight, configuration, density, etc., of PEG) may affect the T_{CH} values. Alternatively, $T_{1\rho(\text{H})}$ is useful for the comparison of local mobility, which is shorter if the polymer chain is less mobile [31].

Figures 7a-c shows the changes in intensities of the methylene carbon signal with variation of contact time (see Figures S10-12 for the raw data). Intensities of the signals increased, reached maximum, and then decreased for all POM-PEG composites. Notably, magnetization decay was the slowest for **CsHPW-PEG1000** (Figure 7a), suggesting that $T_{1\rho(\text{H})}$ is the longest and thus segmental motion of PEG is the highest.

Estimated T_{CH} and $T_{1\rho(\text{H})}$ values are summarized in Table 3. $T_{1\rho(\text{H})}$ for **CsHPW-PEG1000** (1.6 ms) was larger than that of **CsHSiW-PEG1000** (1.0 ms) suggesting that PEG1000 in **CsHSiW-PEG1000** is less mobile, which is probably due to the larger electrostatic interaction between PEG and the constituent ions. $T_{1\rho(\text{H})}$ values for **CsHPW-PEG m** decreased with increase in m from 1000 (1.6 ms) to 12000 (6.0×10^{-1} ms), suggesting that segmental motion of PEG decreased with increase in molecular weights. Since the trends in $T_{1\rho(\text{H})}$ values fairly agree with

that of proton conductivities, proton hopping in the crystal lattice of POM-PEG composites is probably assisted by the segmental motion of PEG.

4. Conclusion

Crystalline POM-PEG composites aimed as non-humidified intermediate-temperature proton conductors were synthesized. Among the POM-PEG composites, **CsHPW-PEG1000** possessed one-dimensional channels with diameters of ca. 6 and 8 Å, where PEG probably resided, and showed the best performance as a proton conductor (1.2×10^{-5} S cm⁻¹ at 443 K). Effects of molecular weights of PEG and anion charges were investigated, and the results implied that amount of H⁺ is not the primary factor in proton conduction of POM-PEG composites. Variable contact time ¹³C-CPMASNMR revealed that local mobility (i.e., segmental motion) of PEG is related to the trends in proton conductivities. These results suggest that segmental motion of PEG assists the proton hopping among POMs in the crystal lattice of POM-PEG composites. While we succeeded to incorporate hydrophilic POMs into anhydrous hydrophobic crystalline compounds with a proton conducting pathway (polymer), proton conductivities of the POM-PEG composites were not high enough. Trials to increase the segmental motion of the polymer are in progress.

Supplementary information

IR spectra (Figure S1). ¹H-MASNMR spectrum of **CsHPW-PEG1000** (Figure S2). Water sorption isotherm of **CsHPW-PEG1000** (Figure S3). ¹³C-MASNMR spectrum of **CsHPW-PEG12000** (Figure S4). Crystal structure of Cs₃PW₁₂O₄₀ (Figure S5). TG-DTA data of **CsHPW-PEG12000** (Figure S6). Arrhenius plot of proton conductivities of **CsHPW-PEG1000** (Figure S7). ¹H-MASNMR spectrum of **CsHSiW-PEG1000** (Figure S8). Powder XRD patterns of **CsHSiW-PEG1000** (Figure S9). ¹³C-CPMASNMR spectra (60–80 ppm) of POM-PEG

composites with variation of contact time (Figures S10-12). X-ray data for **CsHPW-PEG1000** (CCDC-1051215) and **CsHSiW-PEG1000** (CCDC-1051217). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

Acknowledgement

This work was supported by JST-PRESTO and Grant-in-Aids for Scientific Research from the Ministry of Education, Culture, Science, Sports, and Technology of Japan. Prof. Motoyuki Matsuo and Dr. Katsumi Shozugawa (Univ. of Tokyo) are acknowledged for providing access to the ICP instrument. Mr. Shotaro Magira (Univ. of Tokyo) is acknowledged for checking the contents of the manuscript.

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Table 1. Crystal data

	CsHPW-PEG1000	CsHSiW-PEG1000
Crystal system	monoclinic	orthorhombic
Space group	<i>C2/c</i>	<i>Ibca</i>
Unit cell dimensions	$a = 27.85(6)$ $b = 24.91(4)$ $c = 15.12(5)$ $\beta = 102.45(8)$	$a = 27.823(7)$ $b = 27.836(7)$ $c = 33.489(9)$
Volume	10239(42)	25936(12)
<i>Z</i>	4	8
$R_1(I > 2\sigma(I))$	0.0520	0.1200
wR_2	0.1352	0.3687
GOF	0.907	1.041

Table 2. Proton Conductivities ($\times 10^{-6} \text{ S cm}^{-1}$) of POM-PEG composites

	CsHPW-PEG1000	CsHPW-PEG12000	CsHSiW-PEG1000
403 K	3.2×10^{-1}	-	9.3×10^{-2}
413 K	1.1	-	3.0×10^{-1}
423 K	2.0	4.1×10^{-2}	-
433 K	5.2	9.6×10^{-2}	-
443 K	12	2.1×10^{-1}	-

Table 3. T_{CH} and $T_{1\rho(H)}$ values (ms) of POM-PEG composites

	CsHPW-PEG1000	CsHPW-PEG12000	CsHSiW-PEG1000
T_{CH}	4.5×10^{-2}	1.0×10^{-1}	5.5×10^{-2}
$T_{1\rho(H)}$	1.6	6.0×10^{-1}	1.0

Figure 1. (a) Ball and stick and (b) space filling model of the crystal structure of **CsHPW-PEG1000** in the *ab* plane. The large and small circles in (b) show the one-dimensional channels with diameters of 6 and 8 Å, respectively.

Figure 2. (a) ^{13}C -MASNMR spectrum (single pulse excitation with ^1H -decoupling) and (b) TG-DTA of CsHPW-PEG1000.

Figure 3. Powder XRD patterns of (a) **CsHPW-PEG1000** (calculated), (b) **CsHPW-PEG1000** (experimental), and (c) **CsHPW-PEG12000** (experimental). Powder XRD patterns of **CsHPW-PEG1000** (experimental) after heating at (d) 423 K and (e) 453 K. (f) Powder XRD pattern of $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ (calculated).

Figure 4. Nyquist plots of the impedance spectra of **CsHPW-PEG m** . $m =$ (a) 1000 and (b) 12000. Blue, green, purple, and red plots show the data at 413, 423, 433, and 443 K, respectively.

Figure 5. (a) Ball and stick and (b) space filling model of the crystal structure of **CsHSiW-PEG1000** in the ab plane.

Figure 6. (a) ^{13}C -MASNMR spectrum (single pulse excitation with ^1H -decoupling), (b) TG-DTA, and (c) Nyquist plots of the impedance spectra of **CsHPW-PEG1000**.

Figure 7. Changes in the intensities of the methylene carbon signal with variation of contact time. (a) **CsHPW-PEG1000**, (b) **CsHPW-PEG12000**, and (c) **CsHSiW-PEG1000**. Experimental and calculated (from eq.1) data are shown by the black circles and red lines, respectively. Intensities are normalized by the largest signal in each plot.