Proton-conductive membranes based on vanadium substituted heteropoly acids with Keggin structure and polymers

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ABSTRACT: In this article, novel proton-conducting composite membranes SPEEK/PW$_{11}$V and PVA/SiW$_{11}$V were synthesized from vanadium substituted heteropoly acids (H$_4$PW$_{11}$VO$_{40}$·8H$_2$O and H$_5$SiW$_{11}$VO$_{40}$·15H$_2$O, abbreviated as PW$_{11}$V and SiW$_{11}$V) and polymers (SPEEK or PVA) at the weight ratio 70 : 30. The membranes were characterized by the infrared spectroscopy, X-ray powder diffraction, and scanning electron microscopy, which confirmed the maintenance of the Keggin framework and dispersion homogeneously in the polymer matrix without long-range ordering. Their proton-conducting properties were investigated with electrochemical impedance spectroscopy. The results show that the respective proton conductivities of SPEEK/PW$_{11}$V and PVA/SiW$_{11}$V membranes were in the order of 10^{-2} and 10^{-4} S cm^{-1} at ambient temperature. The temperature dependence of the two composite membrane electrolytes exhibit Arrhenius behavior, and the observed activation energies to be 15.82 kJ mol^{-1} for SPEEK/PW$_{11}$V and 14.40 kJ mol^{-1} for PVA/SiW$_{11}$V, which indicates that the proton conduction complies with the Grotthuss mechanism. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42204.

INTRODUCTION

Proton-conducting solids are of interest for a broad range of applications, such as proton sensor, separation, acidic catalyst, and most importantly high-efficiency electrochemical energy conversion in fuel cells. With growing concerns on the depletion of petroleum-based energy resources and climate change, renewable energy systems have been considered as a key technology for solving global environment and energy problems by reducing emission from fossil fuels. Polymer electrolyte membrane fuel cells (PEMFCs), a source of electrical power for transportation, residential and portable applications, were extensively researched in recent years due to their high efficiency, clean production and low-temperature operation.[1–3] Polymer electrolyte membrane (PEM) is recognized as the key element among the primary components to improve fuel cell durability, performance as well as cost-effective to ensure sustainable commercialization of polymer electrolyte fuel cells.[4] Currently, the most advanced membranes are based on the perfluorosulfonic acid, such as Nafion®. These combine the required chemical, electrochemical, and mechanical stability with high proton conductiv-

ity. However, they are inherently expensive, sensitive to dehydration at elevated temperatures (>80°C) and show considerable methanol permeability, which limited their performance and commercialization. So, research on cost-effective high-performance electrolyte materials has been active in the entire course of fuel cell development. Several methods have been proposed for the development of alternative membranes. Incorporation of hydrophilic oxides was pursued extensively, and the introduction of inorganic proton donors into the polymer electrolyte matrix increases various properties of the polymer electrolyte such as proton conductivity, thermal stability, and therefore, it gained a lot of attention due to their excellent performance in various aspects. Recently, organic–inorganic hybrid materials based on polymers and inorganic proton-conductors, such as heteropoly acids (HPAs), have been considered as electrolyte membranes for fuel cell operations.[5]

HPAs are nanosized polynuclear metal-oxygen clusters with interesting conductivity, catalytic, and many other properties.[6–9] They are one of the best proton conductive materials among the inorganic solid electrolytes. Since the late 1970s, when

Nakamura *et al.* first reported that the electrical conductivities of $H_3PM_{12}O_{40} \cdot 29H_2O$ (M = Mo, W) are larger than those of other proton conductors, HPAs of various composition and their salts have been frequently investigated.[10–14] Because of their structural diversity and sensitive to surrounding conditions: relative humidity, partial pressure of hydrogen, and temperature, these materials are particularly suitable for incorporation into a wide variety of membrane materials for which they can be specifically tailored. HPAs have become one of the most promising additives to improve the conductivity of PEMs under drier and hotter conditions, due to their high intrinsic ionic conductivity in the solid state, their favorable interactions with the ionomer, their ability to increase the local proton concentration, and their favorable impact on forming hydrogen bonding networks.[15]

The high proton conductivity of HPA and its potential interactions with a host material can be understood by considering its structure. Solid HPAs possess a discrete ionic structure comprising fairly mobile basic structural heteropolyanions and countercations (H^+, H_3O^+, $H_5O_2^+$, etc.). The most common local structure is the Keggin form, which consists of a central tetrahedron XO_4 (X = P, Si, etc.) surrounded by four M_3O_{13} (M = W or Mo) sets formed by three edge-sharing octahedral. The M^{6+} ions can be substituted by many other metal ions, for example, V^{5+}, Co^{2+}, Zn^{2+}, etc. This structure is frequently preserved upon substitution or oxidation/reduction and manifests itself to exhibit extremely high proton mobility and "pseudo-liquid phase" behavior.[16] It is attributed to the large size of the polyanion, which has a low and delocalizable surface charge density, thus weaken the attraction of the proton to the anion, as found in liquid superacids. Structure and properties of HPAs exist in a series of hydrate phases, of which the stable forms depend on temperature and relative humidity. Two types of protons have been found in HPA hydrates: (1) non-localized hydrated protons bound to one heteropolyanion as a whole and rapidly exchanging with the protons of the water molecules in the hydration shell of the acid; (2) non-hydrated, less mobile protons localized at the peripheral oxygen atoms of the polyanion. The proton positions may be different because they are determined not only by the negative charge on the oxygen atoms of the polyanion but also by the character of the packing and the unit cell parameters.[17] Consequently the proton conductivity depends on the number of water molecules coordinated to the Keggin unit and varies with heteroatom, polyatom, and polyanion.[18–20]

Over the last few decades, Many papers have been published concerning polymer electrolyte membranes composited with Keggin-type HPAs, in particular the most typical ones such as $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$. However, there has been very little exploitation of the other forms of HPA to modify these conductive composite membranes. Transition metal substituted HPAs have more negative charge of the heteropolyanion, and larger number of protons in their structure as compared to the parent acids. They can also release mobile protonic carriers to afford the conductivity of the membrane. This study was conducted for the first time to investigate the composite membranes based on vanadium substituted heteropolyacids ($H_4PW_{11}VO_{40} \cdot 8H_2O$ and $H_5SiW_{11}VO_{40} \cdot 15H_2O$, abbreviated
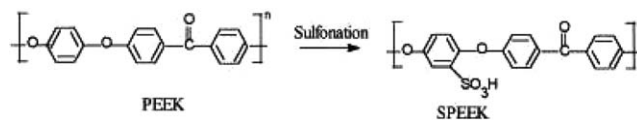

Figure 1. Structure of PEEK and SPEEK.

as $PW_{11}V$ or $SiW_{11}V$) and polymers. Partially sulfonated polyether ether ketone (SPEEK) and polyvinyl alcohol (PVA) have excellent chemical resistance, high thermo-oxidative stability and low cost. They are proper organic polymers in which to immobilize HPAs and provide functional groups that aid in ion mobility.[21–23] The preparation procedure, structural characterization, and conductive performance of the membranes SPEEK/$PW_{11}V$ and PVA/$SiW_{11}V$ are presented in this article. It was demonstrated that the presence of HPAs leads to an enhancement of the membrane conductivity, without detriment to their flexibility.

EXPERIMENTAL

Instrument and Reagent

Infrared (IR) spectrum was recorded on a NICOLET NEXUS 470 FT/IR spectrometer over the wave number range 400–4000 cm^{-1} using KBr pellets. X-ray powder diffraction (XRD) analysis was obtained on a BRUKER D8 ADVANCE X-ray diffractometer using a Cu tube operated at 40 kV and 40 mA in the range of $2\theta = 4$–40° at a rate of $0.02° s^{-1}$. A JSM-6700F was used for studying the morphology of membranes. Conductivity measurements were taken by a four-point-probe method using AC impedance spectroscopy over a frequency range of 10 mHz–100 kHz, 10 mV AC perturbation and 0.0 V DC rest voltage. A sheet of membrane (4×1 cm^2) was placed in the test cell.

PEEK was obtained from Chemistry of Jilin University. PEEK can be functionalized by sulfonation and the DS can be controlled by reaction time and temperature. The chemical structure of PEEK is shown in Figure 1.

PVA (DP = 1750 ± 50) was purchased from Sinopharm Chemical Reagent. The chemical structure of PVA is shown in Figure 2. All reagents were analysis grade.

Preparation of Polymers

The sulfonation of PEEK was performed similarly to the procedures reported in the literature.[24] PEEK was dried in a vacuum oven at 100°C overnight. Thereafter, 3 g of polymer was dissolved in 30 mL of a mixture of concentrated and fuming sulfuric acids (volume ratio: 1 : 1), and vigorously stirred at room temperature for 5 days. Then the viscous solution was quenched in ice water and agitated mechanically. The agitation was continued 1 h further and then the polymer suspension was left to settle overnight. The polymer precipitate was filtered and washed several times with distilled water until the pH was
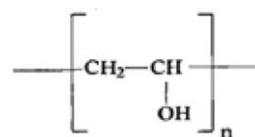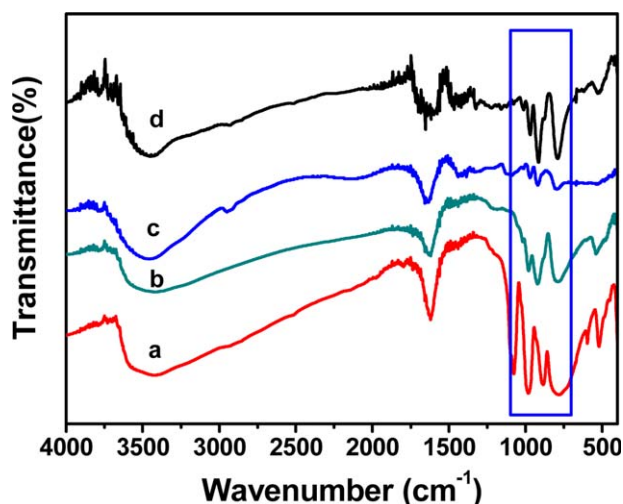

Figure 2. Structure of PVA.

Figure 3. IR spectra of $PW_{11}V$ (a), $SiW_{11}V$ (b), $PVA/SiW_{11}V$ (c), and $SPEEK/PW_{11}V$ (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

neutral. The polymer was then dried under vacuum for 8–10 h at 100°C. The final product is the sulfonic acid form of PEEK (SPEEK).

Preparation of the Hybrid Membrane

$H_4PW_{11}VO_{40} \cdot 8H_2O$ was synthesized by the literature method.[25] SPEEK (0.15 g) was first dissolved in dimethylformamide (DMF) and 0.35 g of powdered $PW_{11}V$ was then added to the solution. The resulting mixture was stirred for 24 h. After evaporation of most of the solvent the mixture was cast onto a glass plate using a casting knife. The cast membranes were dried at room temperature overnight. The pure SPEEK membrane was prepared at the same time for comparison. The thickness of the pure SPEEK and $SPEEK/PW_{11}V$ membrane is 82 μm and 31 μm, respectively.

$H_5SiW_{11}VO_{40} \cdot 15H_2O$ was synthesized by the stepwise acidification and the stepwise addition of element solutions.[26] PVA (0.60 g) was dissolved in 5 mL of boiling water, then $H_5SiW_{11}VO_{40} \cdot 15H_2O$ (1.40 g) were added to the solution, and the mixture was stirred at 60°C for about 3 h. The viscous solution was equably spread over the plastic flat with desirable thickness and dried at room temperature. The thickness of the pure PVA and $PVA/SiW_{11}V$ membrane is 18 μm and 33 μm, respectively. These membranes are flexible, yellowish, transparent, and homogeneous.

RESULTS AND DISCUSSION

IR Spectra

The comparative IR spectra of $PW_{11}V$, $SiW_{11}V$, $SPEEK/PW_{11}V$, and $PVA/SiW_{11}V$ are presented in Figure 3. The main bands are assigned and tabulated in Table I. In the wavenumber region from 700 to 1100 cm^{-1}, the fingerprint vibrational bands of Keggin anions are also observed in the spectrum of the composite membranes. The pure $PW_{11}V$ presents four bands of vibration, the peaks at 1078, 984, 890, and 795 cm^{-1} were ascribed as the stretching modes of $P—O_a$, $M=O_d$, $M—O_b—M$, and $M—O_c—M$ bonds, respectively (curve a). The corresponding

characteristic bands of $SiW_{11}V$ appear at 923, 980, 876, and 784 cm^{-1} (curve b). The positions of vibration modes of all types of M—O bonds are strongly influenced by interaction of HPAs with the polymer matrices. Generally, the $M—O_d$ stretching can be considered as pure vibration and is an increase function of the anion–anion interaction. The band of $M—O_d$ has a red shift from 984 ($PW_{11}V$) to 978 cm^{-1} ($SPEEK/PW_{11}V$), and 980 ($SiW_{11}V$) to 970 cm^{-1} ($PVA/SiW_{11}V$), which is attributed to the weakening of anion–anion interactions of the electrostatic type. The stretching involving O_b or O_c atoms presents mixed bending-stretching character. As a result, these frequency shifts of $M—O_b—M$ and $M—O_c—M$ may show different changes. The $M—O_b—M$ vibration is both red shifted, from 890 ($PW_{11}V$) to 884 cm^{-1} ($SPEEK/PW_{11}V$), and 876 ($SiW_{11}V$) to 854 cm^{-1} ($PVA/SiW_{11}V$), while that of $M—O_c—M$ is shifted in different directions, from 795 ($PW_{11}V$) to 785 cm^{-1} ($SPEEK/PW_{11}V$), and 784 ($SiW_{11}V$) to 803 cm^{-1} ($PVA/SiW_{11}V$).

In addition, the stretching vibration of the tetrahedral $X—O_a$ bonds has a slight shift, from 1078 ($PW_{11}V$) to 1080 cm^{-1} ($SPEEK/PW_{11}V$), and 923 ($SiW_{11}V$) to 919 cm^{-1} ($PVA/SiW_{11}V$). These peak frequency shifts may be associated with intermolecular interaction between the polar groups of polymers (—SO_3H or —OH) and HPAs, and by much greater hydration. Nevertheless, the existence of the HPA-matrix interaction did not affect the Keggin structure, which is maintained undegradable during the preparation.

In the higher wavenumber region, the HPAs exhibit two other peaks at around 3403 and 1610 cm^{-1}. These are assigned to the stretching mode of O—H bonds and the bending mode of H—O—H bonds, respectively. Such peaks possibly arise from the physically adsorbed H_2O and/or the H_2O existing around the heteropolyanions. For the composite membrane $SPEEK/PW_{11}V$, the appearance of a broad band around 3450 cm^{-1} was assigned to O—H vibration from sulfonic acid groups interacting with water molecules. The absorption at 1652 cm^{-1} was attributed to stretching vibrations of backbone carbonyl group. The aromatic C—C band was observed at 1470 and 1493 cm^{-1} due to the substitution upon sulfonation. The other bands are due to sulfur-oxygen vibrations: asymmetric O=S=O stretch (1252 cm^{-1}), symmetric O=S=O stretch (1080 cm^{-1}), S=O stretch (1024 cm^{-1}) and S—O stretch (709 cm^{-1}).[27] The characteristic bands of pure PVA can be also observed in the composite membrane $PVA/SiW_{11}V$, which are located at 3470, 2960, 1640, 1470, and 1396 cm^{-1}, and assigned to O—H stretching, —CH_2 stretching, H—O—H bending, —CH_2 bending and C—O

Table I. Data of IR Spectra for the Materials

| Material | Vibration frequency (cm^{-1}) | | | |
	ν_{as} (W-O_d)	ν_{as} (X-O_a)	ν_{as} (W-O_b-W)	ν_{as} (W-O_c-W)
$PW_{11}V$	984	1078	890	795
$SiW_{11}V$	980	923	876	784
$SPEEK/PW_{11}V$	978	1080	884	785
$PVA/SiW_{11}V$	970	919	854	803
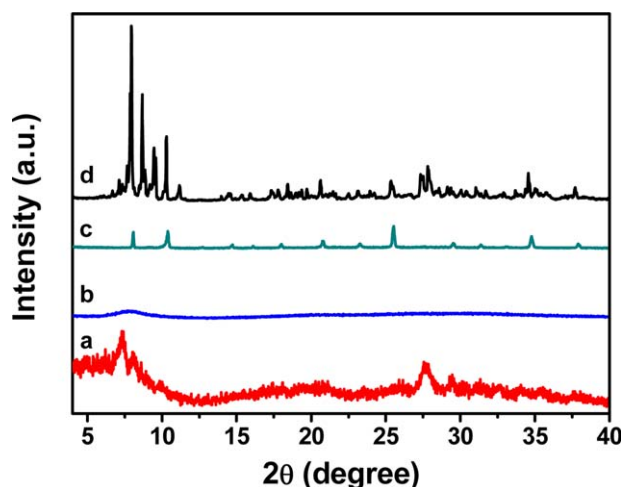
Figure 4. XRD of SPEEK/PW$_{11}$V (a), PVA/SiW$_{11}$V (b), SiW$_{11}$V (c), and PW$_{11}$V (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stretching, respectively.[28] It shows that the organic matrix has not been destroyed during the composite process.

X-ray Diffraction Patterns

The microstructure of the composite membranes could be revealed from XRD measurement. As shown in Figure 4, The X-ray powder diffraction patterns of these membranes show few and broad reflections characteristic of an amorphous state as compared to highly crystalline nature of PW$_{11}$V or SiW$_{11}$V. This is the effect of finely dispersed HPA in the polymer matrix. An obvious peak exists at $2\theta = 5$–$10°$, indicating that the HPA is dominant and its crystalline structure still remains.

Scanning Electron Microscopy

Surface morphology of the composite membranes SPEEK/PW$_{11}$V (a) and PVA/SiW$_{11}$V (b) were investigated as shown in Figure 5. By virtue of elastomeric property of SPEEK, there is not much visible evidence representing that the presence of HPAs in the image was observed, suggesting that PW$_{11}$V was highly dispersed as fine particles in the polymer matrix although some agglomerations were observed in some part of the image [Figure 5(a)]. The composite membrane PVA/SiW$_{11}$V show spherical particles dispersed uniformly in the polymer matrix [Figure 5(b)]. The result supports the specific interaction between HPAs and polymers. This homogeneous distribution will be favorable for proton transport as it minimizes the distance between particles. This statement was also supported by the IR spectra and XRD patterns as mentioned above.

Conductivity

The proton conductivity plays an important role in the fuel cell membranes. Figure 6 shows Nyquist plots for the PVA (a), SPEEK (b), PVA/SiW$_{11}$V (c), and SPEEK/PW$_{11}$V (d) at 25°C and 71% relative humidity. The impedance plots of the samples show a high-frequency semicircle and a low frequency inclined line. The semicircle arises from coupled resistance/capacitance (R/C) at the electrolyte/electrode interface and the inclined line is due to the effect of the blocking electrodes.[29] The proton

conductivity (σ, S cm^{-1}) of membranes was calculated using the following equation:

$$\sigma = \frac{L}{RS} \qquad (1)$$

where L was the distance between the electrode pairs, S was the cross-sectional area of the membrane, and R was resistance of the membrane (obtained from the intercept to the real axis). The figures show that the proton conductivity of SPEEK, SPEEK/PW$_{11}$V, PVA, and PVA/SiW$_{11}$V is 1.09×10^{-4}, 1.84×10^{-2}, 3.34×10^{-7}, and 3.44×10^{-4} S cm^{-1}, respectively. It indicates that the conductivity of composite membranes are superior to the pristine polymers and correspondingly, the SPEEK/PW$_{11}$V was more favorable for obtaining high conductivity due to the higher number of acid sites. It is known that the hydrophilic/hydrophobic phase separation of SPEEK is narrower and more branched with less hydrophilic interconnection channels passing through hydrophobic domains. This minimizes the water uptake as well as swelling in SPEEK membrane. Incorporation of PW$_{11}$V to the polymer matrix caused the increment of conductivity and the aqueous phase more continuous due to the intermolecular hydrogen bonds. PVA has excellent insulation property as polymer materials. The proton conductivity of plain PVA membrane was in the order of 10^{-7} S cm^{-1}. The reactive —OH groups in polymer chain tend to form intramolecular hydrogen bonds. Addition of SiW$_{11}$V content to the PVA
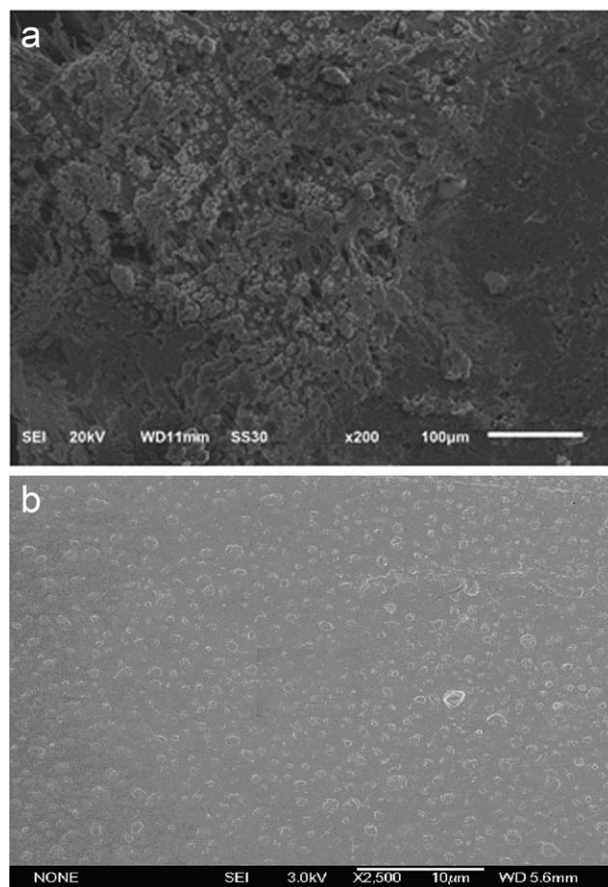

Figure 5. SEM micrograph of the composite membrane SPEEK/PW$_{11}$V (a) and PVA/SiW$_{11}$V (b).
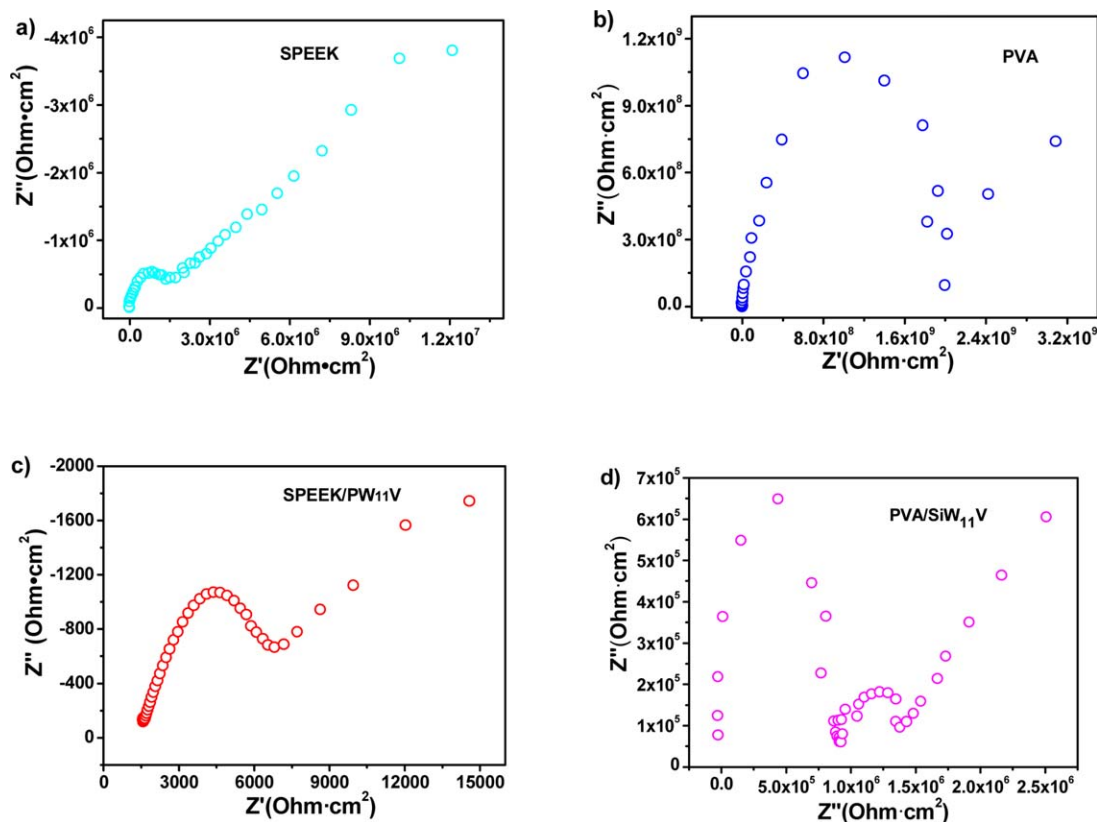
Figure 6. Electrochemical impedance spectroscopy of SPEEK (a), PVA (b), SPEEK/PW$_{11}$V (c), and PVA/SiW$_{11}$V (d) at ambient temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solution results in more intermolecular hydrogen bonds and increases free volumes. This causes the conductivity of PVA/SiW$_{11}$V membrane increased up to 10^{-4} S cm^{-1} order.

The variation of conductivity with temperature is in accordance with the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(-E_a/\kappa T\right) \qquad (2)$$

where E_a denotes the activation energy of the conductivity, σ_0 is the pre-exponential factor, and κ is the Boltzmann constant. Figure 7 shows the Arrhenius plots of proton conduction. The activation energy calculated from the slope is 15.82 kJ mol^{-1} for SPEEK/PW$_{11}$V and 14.40 kJ mol^{-1} for PVA/SiW$_{11}$V, which is lower than that of pure PW$_{11}$V (25.66 kJ mol^{-1}) and SiW$_{11}$V (21.59 kJ mol^{-1}). The result indicates that these membranes conductivity is dominated by Grotthuss mechanism. The resistance of the membrane decreases with the increasing temperature, because the proton transport paths turn more perfect and more protons were produced with the increasing temperature.[30] Further the vibrational motion of the polymer backbone and side chains, which becomes more vigorous with increase in temperature can also facilitate the conduction of ions.[31]

Figure 8 represents proton conduction in the network structure of the composite membranes. The density of the Keggin structure is very high, which may involve clustering or agglomeration. Clustered ionomers absorb more water; therefore, a large increase in water uptake results from the presence of ion-rich regions where proton transfer is particularly fast. In the SPEEK/PW$_{11}$V

membrane (a), the proton conduction is promoted by the proton transfer through the fraction of hydrophilic region (ionic clusters), or from the protonated —SO$_3$H to a nonprotonated —SO$_3$H;[32–34] while in the membrane PVA/SiW$_{11}$V (b), protons transfer within a network of hydrogen bonds, where the H$_3$O$^+$ cations interacted with the oxygen of the PVA chains and/or the oxygen of the Keggin anions. It was concluded that the proton conductivities of the described new composite membranes are
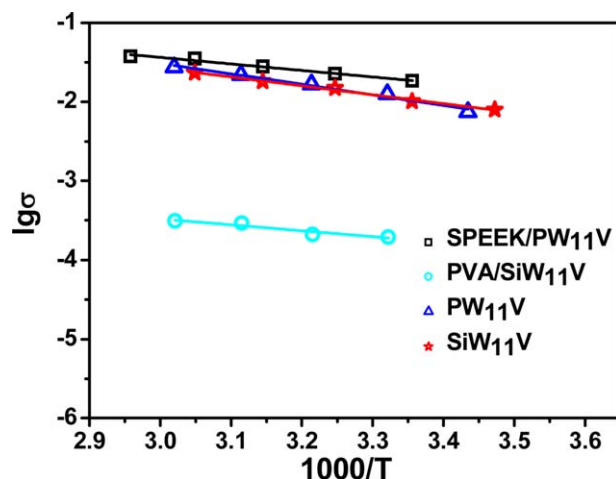

Figure 7. Arrhenius plots of pure PW$_{11}$V, SiW$_{11}$V, PVA/SiW$_{11}$V, and SPEEK/PW$_{11}$V membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
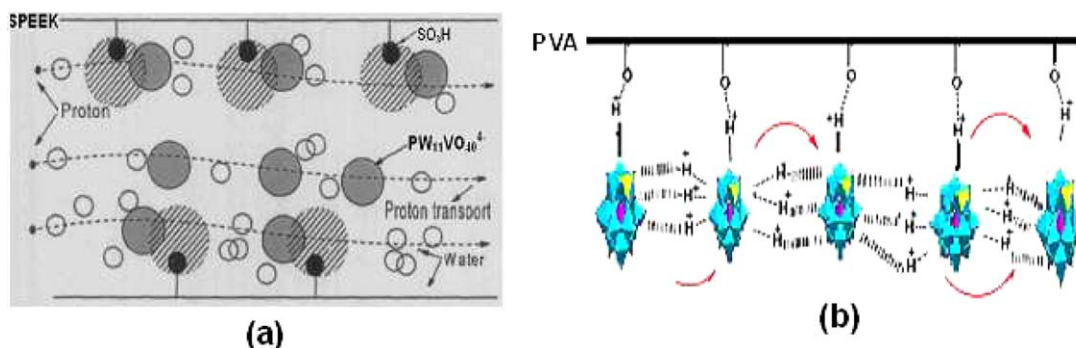
Figure 8. Proton conduction in the network structure of the composite membranes: SPEEK/PW$_{11}$V (a); PVA/SiW$_{11}$V (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

closer or better than that of the composite membranes embedded with H$_3$PM$_{12}$O$_{40}$·29H$_2$O (M = W, Mo).[24,35] The substituted HPAs, PW$_{11}$V, and SiW$_{11}$V, are suitable membrane fillers for increasing the number of protonic carriers and improving the hydrophilic character of the membranes. These prospective membranes might be preferable in certain cases as an interesting and potential alternative proton conducting PEMs.

CONCLUSIONS

As far as low-temperature conductors are concerned, the most impressive results in terms of conductivity improvement are reported for novel composite membranes based on vanadium substituted HPAs (PW$_{11}$V and SiW$_{11}$V) and polymers (SPEEK or PVA). The SPEEK/PW$_{11}$V and PVA/SiW$_{11}$V membranes are freestanding, flexible, yellowish, and transparent. These composite membranes exhibit better conductivity values than the corresponding pure polymers. A maximum conductivity of the order of 10^{-2} S cm^{-1} was obtained at ambient temperature for the SPEEK/PW$_{11}$V membrane. Similarly, the addition of SiW$_{11}$V content increases the conductivity of PVA membrane to 10^{-4} S cm^{-1} order. The activation energy is 15.82 kJ mol^{-1} for SPEEK/PW$_{11}$V and 14.40 kJ mol^{-1} for PVA/SiW$_{11}$V, indicating that the proton transfer in the membranes proceed predominantly by the Grotthuss mechanism. These economical membranes can offer opportunities of replacing expensive perfluorosulfonic acid polymer membranes in the electrochemical devices such as PEMFCs. This work lays a solid foundation for further development in the special fields of study.

ACKNOWLEDGMENTS

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