



## Enhanced conductivity and electrochemical properties for class of hybrid systems via sol–gel techniques

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### ABSTRACT

Enhanced high proton-conducting hybrid membranes were prepared via the sol–gel technique using phosphotungstic acid (PWA) mixed with polyvinylalcohol (PVA) and phosphosilicate ( $P_2O_5/SiO_2$ ). These new class of membranes showed excellent proton conductivities and were confirmed to be promising electrolytes for fuel cells. Moreover, their mechanical, thermal, swelling and structural properties were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal analysis, and swelling measurements. Also proton conductivity and electrochemical studies were performed. The materials were thermally stable up to 300 °C, and the swelling capability was found to be increased by addition of the  $SiO_2$  function. The phosphosilicate mixed with poly(vinylalcohol) (PVA) and heteropolyacid thus gave rise to the creation of a strong PVA/PWA/ $P_2O_5/SiO_2$  hybrid membrane network through Keggin ions.

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### 1. Introduction

The use of fuel cells in both stationary and mobile power applications can offer significant advantages for the sustainable conversion of energy. Benefits arising from the use of fuel cells include efficiency and reliability. Despite the promise of the proton exchange membrane fuel cell (PEMFC) technology, important materials design and system engineering challenges still exist, preventing commercialization. From a materials perspective, proton exchange membranes capable of operating at low or intermediate temperatures need to be developed.

Heteropolyacids (HPAs) have been largely employed as catalysts in heterogeneous reactions due to their unique structural and chemical properties. Solid inorganic proton conductors like zirconium phosphates, heteropolyacids (HPAs), and metal hydrogen sulfates have dual roles of being both hydrophilic and proton conducting. Consequently, a major research objective is to fix the HPAs in stable structures by forming composites [1–4] that are able to maintain their high proton conductivity. A composite matrix reduces the leaching of HPA.

The heteropolyacid also acts as a catalyst for hydrolysis/condensation reaction of the precursor. These membranes have been studied in order to gain knowledge of the interaction of the HPA with the polymer to enable a full understanding of this beneficial

interaction. During the last decades, several synthesis routes have been proposed in order to obtain suitable proton exchange membranes for low-temperature fuel cells.

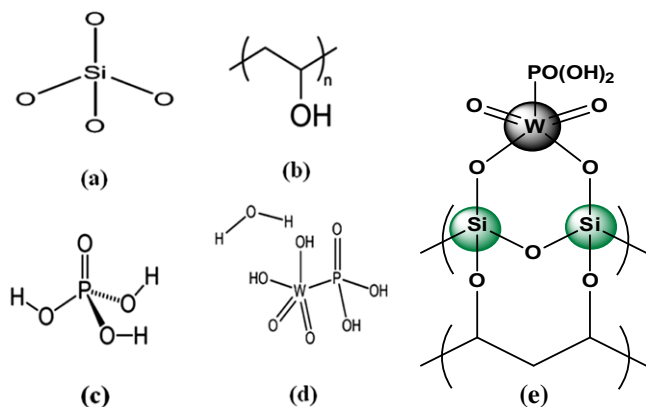
A variety of membranes based on polymer blends, cross-linked polymers or polymer-ceramic composites are available [5,6]. In addition, more and more efforts have been devoted to improving the proton conductivity of solid polymer electrolytes. Many proton-conducting membranes based on blends of polymer and inorganic acids (such as  $H_2SO_4$  and  $H_3PO_4$ ) have exhibited very good proton conductivities [7–11]. Studies on PVA-based systems have shown that they present a decent good proton conduction and that they can be applied in fuel cells [12–20]. Also poly(vinyl alcohol) blended with inorganic acids (such as  $H_2SO_4$  or  $H_3PO_4$ ) has demonstrated excellent proton conductivities and optical properties.

Poly(vinylalcohol) is a cheap polymer that fulfills these requirements and, with a high density of functional –OH groups, it also shows potential for chemical cross-linking [21]. PVA is widely used due to its very good adhesion to biological tissues, its biodegradability and its swelling ability [22]. Although from the fuel cell application point of view, an extensive swelling might be detrimental as it reduces the mechanical strength of the membrane and increases the methanol cross-over, the degree of swelling can be controlled and limited by means of partially cross-linking.

Hybrid compounds made by the formation of siloxane (Si–O–Si) bonds are an important body of materials, ranging from inorganic silicates to organically modified polysiloxanes. All of these siloxane-based materials are prepared by hydrolysis and condensation reactions of sol–gel precursors [23]. The homogeneity of the

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**Fig. 1.** The basic chemical structures of (a) TEOS, (b) PVA, (c) H<sub>3</sub>SO<sub>4</sub>, (d) PWA and (e) the hybrid membrane network structure.

inorganic and organic phases allows for molecular engineering of the bulk properties of the hybrid organic/inorganic materials without nanoscale phase separation. The organic group, covalently attached to the silicon atom, can be varied in length, rigidity, geometry of substitution, and functionality.

A main important application of hybrid organic-inorganic material with nano-sized interfaces includes the preparation of membranes for proton exchange membrane fuel cells (PEMFCs) operating at low/intermediate temperatures. Depending on the particular polymer/ceramic filler combination, amorphous or crystalline phases might be promoted [24–26]. The incorporation of an inorganic component to a polymeric one modifies properties like the thermal, chemical and mechanical stability, and proton conductivity. In this case, synthesis was performed of proton-conducting organic/inorganic membranes of phosphotungstic acid mixed with polyvinylalcohol and phosphosilicate. These materials can be polymerized through hydrolysis and condensation reactions to produce a Si–O–Si network. The schematic structure of the composite membranes is shown in Fig. 1. Within them, a silica network was formed in the polymer matrix through self-condensation reactions of the hydrolyzed silanol, which could remarkably decrease the degree of the swelling, and enhance separation properties of the membranes. In this case, PVA/PWA/P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> hybrid membranes were obtained by the sol-gel route, their structural and electrochemical properties were studied, and the results were described.

## 2. Experimental sections

All materials, solvents, deuterated solvents, and reagents were purchased from either Nacalai Tesque or Kishida chemicals and used without further purification. Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (TEOS, 99.9%, Colcote), H<sub>3</sub>PO<sub>4</sub> (reagent grade, Wako), polyvinyl alcohol with a molecular weight of 100,000 g/mol (Nacalai Tesque), and phosphotungstic acid H<sub>3</sub>[P(W<sub>3</sub>O<sub>10</sub>)<sub>4</sub>] (Chameleon Reagent) were used as received. De-ionized H<sub>2</sub>O was purified using a Millipore Gradient Milli-Q® water purification system.

X-ray diffraction (Rigaku, multiflex, Japan) was used for the analysis of the structures of membranes with CuK $\alpha$  radiation generated at 2 kW and 20 mA at a scan rate of 2/min, with the diffraction angle  $2\theta$  ranging from 5 to 90°. Infrared spectra (IR) were measured using a JASCO FTIR-460 spectrometer (spectral range used was 4000–400 cm<sup>-1</sup>). Thermogravimetric (TG)/differential thermal analysis (DTA) measurements were carried out simultaneously on a DTG-50 from Shimadzu instruments. The average pore diameter was measured from gas adsorption analysis (NOVA-1000, Quantochrome). Differential scanning calorimetry (DSC) was performed with a DSC 8000, Perkin Elmer, and a system from TA Instruments, Inc. The measurement was carried out from –50 to 250 °C at a heating and cooling rate of 10 °C/min. Scanning electron microscopy (SEM) images were collected with a Hitachi S-3500N variable pressure scanning electron microscope using an accelerating voltage of 20 kV.

The water uptake of the membrane samples previously dried and weighed was determined after immersion in deionized water at room temperature and weighing every 4 h. The excess water on the sample surface was removed by an absorbent paper, after which the membranes were weighed again, and the uptake (%) was calculated according to Eq. (1):

$$\text{WaterUptake} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100\% \quad (1)$$

where  $M_{\text{wet}}$  and  $M_{\text{dry}}$  are the weight of the wet and dried membranes, respectively.

The preweighed membranes were immersed in deionized water in a closed bottle at room temperature. To achieve equilibrium swelling, they were removed and periodically weighed until the mass weight was constant. Each sample was then wiped off carefully with tissue paper as quickly as possible to remove the surface solution. The amount of absorbed water in the membranes was expressed as the degree of swelling (%<sub>d</sub>) and was calculated according to Eq. (2):

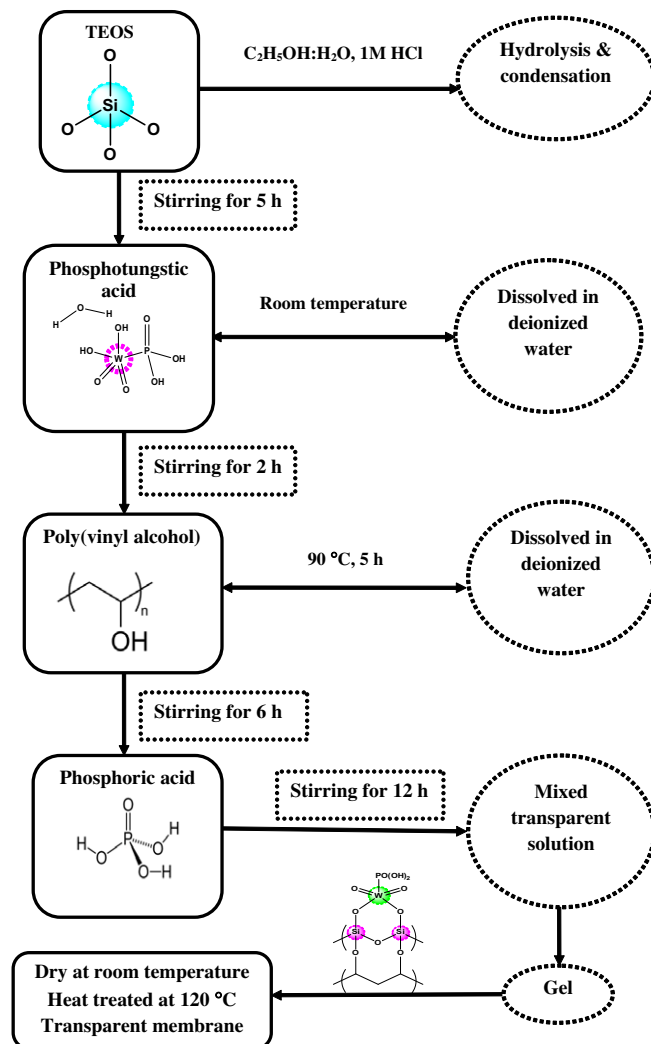
$$\%_d = \frac{d_{\text{wet}} - d_{\text{dry}}}{d_{\text{wet}}} \times 100 \quad (2)$$

where  $d_{\text{wet}}$  and  $d_{\text{dry}}$  are the weights of the swollen and dry membranes, respectively.

The ion exchange capacity (IEC) and sulfonation degree were determined by titration. All the membranes were dried for 6 h at 60 °C under vacuum before being weighed. The membranes were then soaked in 2 M NaCl solution for 2 h to extract all the protons from the membranes. The electrolyte solution was neutralized using a dilute NaOH solution of known concentration. The end-point was detected using phenolphthalein as the indicator. The IEC values were calculated from the number of moles of NaOH used divided by the mass of the dry sample,  $W_{\text{dry}}$ , as given by Eq. (3):

$$\text{IEC} = \frac{V \times M}{W_{\text{dry}}} \quad (3)$$

The proton conductivity was measured with a 1260 impedance analyzer, and an AC impedance technique using a two-probe method, where the AC frequency was scanned from 1 Hz to 1 MHz at a voltage of 100 mV. The cell was composed of two Pt electrodes with 1 cm<sup>2</sup> effective area. The resistance value associated with the membrane conductivity was determined from the high frequency intercept of



**Fig. 2.** Flow chart for the preparation of the PVA/PWA/P<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> hybrid composite membrane.

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