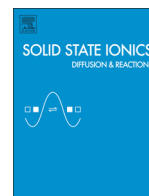




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## Functionalized mesoporous materials as new class high temperature proton exchange membranes for fuel cells

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### ABSTRACT

One of the key components in a proton exchange membrane fuel cell (PEMFC) system is the proton exchange membrane (PEM). PEM not only needs to be highly stable in harsh chemical and physical environment in fuel cells, but also preferably possesses the high proton conductivity at elevated temperature and low humidity conditions to increase the efficiency and simplify the PEMFC power systems. In this paper, the research activity and progresses in the development of heteropolyacids (HPAs) functionalized mesoporous silica as new PEMs for fuel cells are briefly reviewed. HPAs such as  $H_3PW_{12}O_{40}$  or HPW immobilized within the mesoporous silica are highly effective proton transfer carrier. The progresses made so far in this field demonstrate the promising potential of functionalize mesoporous silica nanocomposites in the development of new PEMs for fuel cells operated at high temperatures ( $\sim 200$  °C) and reduced humidity conditions.

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### 1. Introduction

Proton exchange membrane fuel cells (PEMFCs), where chemical energy of fuels such as hydrogen and methanol is directly converted to electrical energy, provide a highly efficient alternative to standard internal combustion engines. PEMFCs have advantages of high power densities, very low greenhouse gas emissions, low-temperature operation, rapid start-up and shut-down times and the ability to use fuels from renewable sources. One of the key components in a fuel cell system is the proton exchange membrane (PEM). The state-of-the-art PEM is the perfluorosulfonic acid (PFSA) polymers like Nafion developed by DuPont due to their good mechanical properties, excellent chemical stability and relatively high proton conductivity at highly hydrated conditions [1]. However, the conductivity of PFSA-based membranes decreases significantly at elevated temperatures ( $\geq 100$  °C) due to the dehydration and degradation of the membranes over 100 °C and at low relative humidity (RH) environment [2–5]. The limited operating temperature complicates water and heat management, requires high-purity hydrogen to avoid CO poisoning of the catalysts and slows electrochemical reactions at electrodes [6–8]. PEMFCs with the capability to operate at high temperatures (100–200 °C) have significant advantages of the high catalytic activity of the electrocatalysts for the  $O_2$  reduction and oxidation reactions of liquid fuels such as

methanol and ethanol, high tolerance of the catalysts to contaminants such as CO and better heat management [7,9].

The emergence of ordered mesoporous silica materials with high structural order, large surface areas and pore volumes, and easy and variable surface functionalization offers great potential as porous frameworks not only for catalyst supports, protein separation, and  $CO_2$  capture [10,11] but also for catalysts' support for fuel oxidation and proton conductor as high temperature PEM applications [12–23]. Marschall et al. [24] synthesized imidazole functionalized mesoporous MCM-41 silica by immersing treatment and the highest conductivity was  $\sim 10^{-4}$  S  $cm^{-1}$  at 140 °C and 100% RH. Research indicated that replacing the pure silica with composite silicate of strong acidity, e.g., the  $Cs_3(H_2PO_4)(HSO_4)_2/SiO_2$  [25],  $CsH_2SO_4-SiO_2$  [26],  $P_2O_5-SiO_2$  [27],  $P_2O_5-TiO_2-SiO_2$  [28] or  $P_2O_5-ZrO_2-SiO_2$  [29] also improves the proton conductivity. Matsushita et al. [30] used HPW and  $SiO_2$  as basic materials and milled them mechanically to form electrolyte and achieved a proton conductivity of  $3 \times 10^{-3}$  S  $cm^{-1}$  at 30 °C and 60% RH. Nogami et al. [18,31–36] incorporated various heteropolyacids into silicaphosphate porous glass and yielded a membrane with proton conductivity of 0.1 S  $cm^{-1}$  at 85 °C and 85% RH. The cell based on HPM and HPW incorporated silicaphosphate glass produced a maximum power of 35–42 mW  $cm^{-2}$  at 30 °C and 30% RH.

We concentrated our efforts on the development of heteropolyacids such as phosphotungstic acid ( $H_3PW_{12}O_{40}$ , abbreviated as HPW)-functionalized mesoporous silica (HPW-*meso*-silica) as new inorganic high temperature PEM for fuel cells [37,38]. The reason for the selection of HPW as proton carrier in the *meso*-silica matrix is twofold, HPW has the highest stability and strongest acidity among the Keggin-type heteropolyacids with a high proton conductivity in fully hydrated state, 0.18 S  $cm^{-1}$  [39] and thermally

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stable up to 500 °C [40]. In this presentation, the synthesis and characteristics of HPW–*meso*-silica nanocomposite as PEMs for fuel cells will be briefly reviewed and the latest development in the HPW–*meso*-silica nanocomposite PEM for the application in the temperature range of 200–300 °C is presented.

## 2. Synthesis of HPW–*meso*-silica nanocomposites

HPW can be incorporated into the mesoporous silica matrix by impregnation or by one-step self-assembly synthesis process, forming immobilized HPW nanoparticles/clusters in the mesoporous silica matrix [37,38]. HPW is soluble in water, forming negatively charged  $\text{PW}_{12}\text{O}_{40}^{3-}$  ions. Under normal conditions, the proton adsorption on the SiOH surface groups of the *meso*-silica is very low. However, the presence of HPW decreases the pH of the precursor as HPW is highly acidic in water and this in turn significantly increases the proton adsorption of

SiOH groups, forming positively charged  $\text{SiOH}_2^+$  [41]. When HPW molecules, silica precursor, and tetraethylorthosilicate (TEOS) are mixed in water, self-assembly occurs between the positively charged silica and the negatively charged HPW by the electrostatic force. With the addition of structure-directing agent, P123, the tube-cumulated mesoporous HPW–silica with the template of P123 surfactant is formed through the cooperative hydrogen bonding and self-assembly between the HPW–silica structure and P123 surfactant [42]. Pluronic P123 is a poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) block copolymer commercially available as amphiphilic polymers. With the phase separation of P123, the colloidal complex forms ordered mesoporous silica with the HPW self-assembled in the mesoporous structure. The surfactant template is then removed by the heat treatment at 400 °C. In the case of HPW impregnated *meso*-silica nanocomposites, *meso*-silica is synthesized by methods reported in the literature [42],

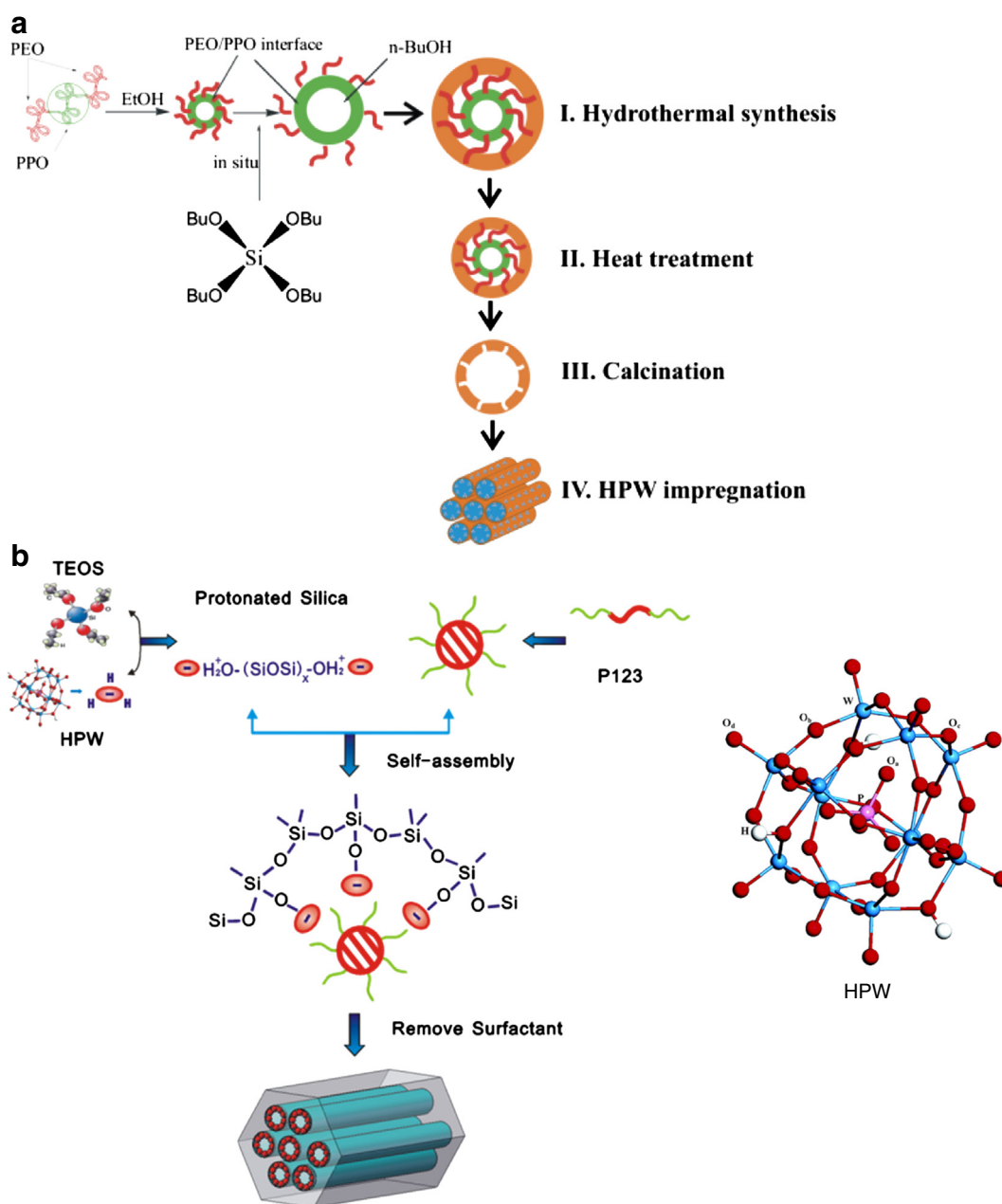


Fig. 1. Schematic of synthesis of HPW–*meso*-silica via (a) two-step HPW impregnation process and (b) one-step self-assembly process.

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