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Polybenzimidazole and sulfonated polyhedral oligosilsesquioxane composite membranes for high temperature polymer electrolyte membrane fuel cells

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ABSTRACT

Composite membranes based on poly(2,2′(*m*-phenylene)-5,5′bibenzimidazole) (PBI) and sulfonated polyhedral oligosilsesquioxane (S-POSS) with S-POSS contents of 5 and 10 wt.% were prepared by solution casting as base materials for high temperature polymer electrolyte membrane fuel cells. With membranes based on pure PBI as a reference point, the composite membranes were characterized with respect to spectroscopic and physicochemical properties. After doping with phosphoric acid, the composite membranes showed considerably improved *ex situ* proton conductivity under anhydrous as well as under fully humidified conditions in the 120-180 °C temperature range. The conductivity improvements were also confirmed by *in situ* fuel cell tests at 160 °C and further supported by the electrochemical impedance spectroscopy data based on the operating membrane electrode assemblies, demonstrating the technical feasibility of the novel electrolyte materials.

1. Introduction

The polybenzimidzoles represent a family of engineering plastics that are well known for their excellent thermo-mechanical properties and chemical stability. In the form of woven fibers they are widely used for heat resistant clothing and in the form of membranes used for a large variety of separation processes [1]. During the last two decades, polybenzimidazole membranes doped with phosphoric acid have also evolved as one of the most promising electrolyte systems for high temperature polymer electrolyte membrane (PEM) fuel cells, especially poly(2,2′(*m*-phenylene)-5,5′bibenzimidazole) (PBI, Figure 1) [2–5].

Compared with the conventional poly(perfluorosulfonic acid) membrane based fuel cells operating at temperatures around 80 °C, the high temperature PEM fuel cells operate in the 120-200 °C range which allows for better catalyst kinetics and fuel impurity tolerance as well as simplified system design [6–9]. A large number of different acids have been considered as PBI dopants and many of them give highly proton conducting systems [10]. Membranes of PBI can also be doped with aqueous bases, which have been proven promising as electrolyte materials for both alkaline fuel cells [11] and recently also for alkaline water electrolysis cells [12]. However, for high temperature PEM fuel cell applications phosphoric acid is of special interest as dopant due to its high thermal stability and low vapor pressure at elevated temperatures. The proton conductivity of phosphoric acid doped PBI membranes increases with increasing acid content, or acid doping level (ADL), which is often defined as the number of phosphoric acid molecules per polymer repeat unit. On the other hand, an increased acid content generally results in reduced mechanical strength due to the strong plasticizing effect of the dopant. Thus a compromise between high proton conductivity and good mechanical strength generally has to be made, and for PBI membranes with a linear average molecular weight of the polymer of 23-33 kg mol^{-1} a practical acid doping level of 5-6 has been suggested [13]. This issue can however to

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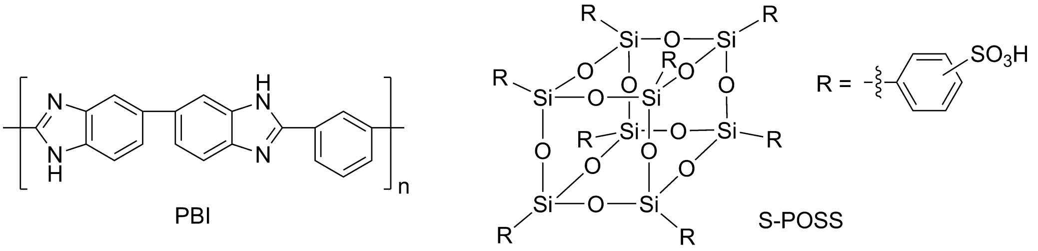

Figure 1. The chemical structure of PBI and S-POSS.

some extent be circumvented by increasing the linear molecular weight of the polymer [14–17] or by generating network structures through different crosslinking concepts [16,18–23] or by developing copolymers [24] or polymer blends [25,26]. This also applies for the pyridine containing poly(arylene ether)s, which is another class of high temperature PEM materials with great potential for fuel cell applications [27]. Another approach to tailor the characteristics of the phosphoric acid doped PBI membranes in terms of e.g. proton conductivity, acid and water retention, dimensional stability and mechanical properties is to introduce a third component through the preparation of organic-inorganic composite systems. Promising results have been demonstrated by introducing hygroscopic inorganic materials such as titanium dioxide [28], modified laponite clay [29] or silica [30,31]. An alternative approach that also has proven successful is to use inorganic solid acids as additives including zirconium phosphates ($Zr(HPO_4)_2{\cdot}nH_2O$, ZrP) [32], phosphotungstic acid ($H_3PW_{12}O_{40}{\cdot}nH_2O$, PWA) [32,33], silicotungstic acid ($H_4SiW_{12}O_{40}{\cdot}nH_2O$, SiWA) [32,34,35], titanium oxysulfate ($TiOSO_4$) [36], boron phosphate (BPO_4) [37] or sulfonated silica [38]. In this way the total acid concentration in the membrane can be increased, often without sacrificing the mechanical stability, which gives higher proton conductivity and thus enhanced fuel cell performance. Sulfonated polyhedral oligosilsesquioxane (S-POSS) is another solid acid based on condensed silica with a cubic cage structure that has been octa-functionalized with phenyl sulfonic acid moieties as shown in Figure 1. This material has proven to enhance the conductivity of composite membranes based on monolayered [39] and multilayered [40] sulfonated poly(phenyl sulfone) membranes for fuel cell applications. The resulting composites showed proton conductivity comparable to that of Nafion® but superior dimensional stability and mechanical strength. Electrospun sulfonated polysulfone composite membranes containing up to 40 wt.% S-POSS have also been proposed as fuel cell electrolytes, showing proton conductivity 2.5 times higher than that of Nafion® and 4.3 times higher than that of the pristine sulfonated polysulfone membrane [41,42]. Targeting a fuel cell operating temperature of 120 °C, ionic liquid imbibed Nafion® and S-POSS composites have proven promising, showing considerably higher proton conductivity than the pure ionic liquid imbibed Nafion® membrane [43]. Other types of sulfonic acid functionalized POSS composite systems based on other polymer matrices such as sulfonated poly(ether ether ketone) [44], polyaniline [45] and crosslinked poly(ethylene glycol) [46] have also recently been investigated as fuel cell electrolytes.

In this work composite membranes based on PBI and S-POSS with S-POSS contents of up to 10 wt.% on the dry non-doped membrane basis were prepared for subsequent doping with phosphoric acid. The novel materials were characterized with respect to *ex situ* chemical and physicochemical properties and tested *in situ* as electrolyte materials for high temperature PEM fuel cells and evaluated based on the polarization data as well as on electrochemical impedance spectroscopy of the MEAs operating at 160 °C, with special emphasis on the voltage losses connected to the ohmic resistance.

2. Experimental

2.1. Materials and membrane preparation

PBI with an inherent viscosity η_{inh} of 0.97 dL g^{-1}, as determined using an Ubbelohde viscometer at 30 °C with a concentration of 5 g L^{-1} in 96 wt.% H_2SO_4, corresponding to a weight average molecular weight M_w of 47 kg mol^{-1} using the empirical Mark-Houwink constants $K = 1.94 \times 10^{-4}$ dL g^{-1} and $\alpha = 0.791$ [47], was synthesized from 3,3′-diaminobenzidine tetrahydrochloride and isophthalic acid by condensation polymerization in polyphosphoric acid and supplied by Danish Power Systems ApS. The PBI powder was subsequently dissolved in *N,N*-dimethylacetamide (DMAc, Aldrich) by reflux at 150 °C to give a 6 wt.% solution.

For the S-POSS synthesis, a dried 1 L 3-necked flask was first charged with octaphenyl POSS® (41.47 g, 40.1 mmol, Hybrid Plastics Inc.) that had been pre-dried *in vacuo*. The flask was equipped with a stirbar, a thermometer, a septum and a condenser with a nitrogen inlet set up to sweep nitrogen past the condenser top. Anhydrous chloroform (170 mL, Acros) was added via a syringe through the septum, and the solidified octaphenyl POSS® was broken up manually into a freely stirring slurry. The flask was cooled with stirring in an ice bath to 1 °C. The septum was replaced with an addition funnel charged with chlorosulfonic acid (32.5 mL, 56.7 g, 487 mmol, 1.5 eq. per phenyl, Sigma-Aldrich), which was added dropwise to the slurry over 50 minutes, keeping the temperature below 3 °C. The resulting clear solution was stirred at room temperature for 4 h and after addition of chloroform (150 mL) the solution was stirred at room temperature overnight. The solution was cooled to 0 °C and 5 mL water (0.3 mol) was added dropwise, producing a white precipitate. The solution was stirred at 0 °C for several hours and placed in a freezer overnight. The cold slurry was vacuum filtered and the light pink solids were crushed in cold chloroform (150 mL), vacuum filtered to dryness, and vacuum dried overnight, yielding 75.6 g pale white solids (S-POSS). The ion exchange capacity (IEC) of the obtained material was 4.5 meq. g^{-1}, as determined through titration with aqueous NaOH on S-POSS dissolved in a mixture of water and tetrahydrofuran (THF) using phenolphthalein as endpoint indicator. The S-POSS was thereafter fully converted into the ammonium salt by dissolving it in a large volume (2 g L^{-1}) boiling demineralized water (due to the very limited solubility of S-POSS in water) followed by titration with aqueous ammonium hydroxide (0.1 mol L^{-1}) until neutral pH during vigorous stirring. The water was subsequently evaporated *in vacuo* at 130 °C to give the ammonium salt of S-POSS as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H (ppm) 7.56-7.63 (m), 7.27-7.36 (m), 7.10 (broad s); ^{13}C NMR (100 MHz, DMSO-d_6): δ_C (ppm) 148.4, 128.4, 127.6, 125.4. An amount of the ammonium salt of S-POSS corresponding to 5 or 10 wt.% (26 and 55 mg, respectively) with respect to the total solid content of the resulting membrane was thereafter mixed with an amount of the PBI/DMAc solution corresponding to 0.5 g PBI. The mixture was ultrasonicated for several hours at slightly elevated temperature (40 °C) to give a visually homogenous casting solution and cast by solvent evaporation at temperatures up