



Polybenzimidazole/strontium cerate nanocomposites with enhanced proton conductivity for proton exchange membrane fuel cells operating at high temperature



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ABSTRACT

In this work, perovskite-type SrCeO₃ nanoparticles were used for improving the properties of high temperature polybenzimidazole (PBI) based proton exchange membranes. Novel proton conducting membrane nanocomposites were prepared using different amounts of SrCeO₃ nanopowders dispersed into PBI by solution casting method. The nanocomposite membranes were studied by using AC impedance spectroscopy, scanning electron microscopy coupled with energy dispersive X-ray and thermo gravimetric analysis. The prepared nanocomposite membranes showed a higher acid uptake, proton conductivity and thermal stability compared with the pure PBI membranes. The highest acid uptake (190%) and proton conductivity (0.105 S/cm at 180 °C and 0% RH) were observed for phosphoric acid-doped PBI nanocomposite membranes containing 8 wt% of SrCeO₃ nanoparticles (PSC₈). The PSC₈ nanocomposite membranes were tested in a fuel cell and the polarization and power curves were obtained at different temperatures. The PSC₈ showed 0.44 W/cm² power density and 0.88 A/cm² current density in 0.5 V at 180 °C. The result obtained from our studies shows the enhanced potential of the PSC₈ as proton exchange membranes for high temperature proton exchange membrane fuel cells.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are composed of an ion exchange membrane sandwiched between two electrode sheets and are being developed for transport applications as well as for stationary fuel cell applications and portable fuel cell applications. Polyperfluorosulfonic acid (PFSA) membranes, such as Nafion are the most widespread type of polymeric membranes used for PEMFCs [1]. But one great weakness of Nafion membranes is their dehydration at temperatures above 80 °C, causing a remarkable decrease in their proton conductivity and mechanical stability. Having high chemical as well as thermal resistance and proton conductivity after doping of polybenzimidazole (PBI) membranes by phosphoric acid (PA) are great options to be

applied in the fuel cells which function at temperatures above 100 °C. The PA doped PBI membrane has been proposed for high temperature PEMFC [2–7]. Nanocomposite membranes are new groups of membranes which include nanoparticles such as SiO₂, TiO₂ and ZrO₂ and other compounds [8–10]. The introduction of nanoparticles especially inorganic oxides into the membranes is expected to improve the proton conductivity but in some cases leads to a decrease in proton conductivity. This improvement is associated with more efficient water management due to the hygroscopic properties of the oxide particles and with the high doping level achieved [11,12]. As mentioned before, the presence of some nanoparticles in PBI nanocomposite membranes results in high proton conductivity in ways such as increase in the water uptake, increase in the amount of doping level and increase in the number of proton conductive functional groups [13].

The acceptor-doped perovskite-type oxides are known as high temperature proton conductors, which are promising materials for devices such as fuel cells [14]. It is known that the proton migrates in the interstitial sites around oxygen ions by hopping in crystals of

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these proton conductor [15,16]. Most of the proton conductors currently under investigations are dependent on or related to water and water indeed plays a vital role in proton conduction processes. Perovskite structures from group II elements such as Sr, Ba and Ra can be used as hygroscopic materials to improve the humidity sensing performance. Due to proton conduction mechanism of these material upon interaction with water, they are well-known to the positive ionic conductors [17]. Doped perovskites have shown good proton conductor properties [18].

Perovskite oxides based on SrCeO_3 have been recognized to exhibit predominate proton conduction under hydrogen containing atmosphere at elevated temperatures [14]. The chemical composition of perovskite oxides could be written as $\text{AB}_{1-x}\text{M}_x\text{O}_{3-\delta}$, where A and B denote two different cations and M is some trivalent elements like rare earth elements and δ is the oxygen deficiency per perovskite unit cell. These perovskite-type ceramics exhibit p-type electronic (hole) conduction under oxidizing atmospheres while they become a proton conductor in the presence of water vapor and hydrogen [19]. The proton conduction in these oxides was directly verified by means of electrochemical transport of hydrogen across the oxides [14,20,21].

Recently, we introduced new proton conducting hybrid membranes based on phenyl or propyl sulfonic acid-functionalized nonporous silica [22,23] and poly(sulfonic acid)-grafted silica nanoparticles [24] for PEM fuel cells. Nafion/ Fe_2TiO_5 nanocomposite membranes were prepared by dispersion of Fe_2TiO_5 nanoparticles within the commercial Nafion membranes [25]. Incorporation of Fe_2TiO_5 nanoparticles in Nafion matrix improved the thermal stability of Nafion membranes which is essential for operation of PEMFCs at elevated temperatures. As mentioned before, it seems that in Fe_2TiO_5 nanoparticles when Fe^{3+} cations are placed near Ti^{4+} cations, the acidic character of these ions is increased. Fe_2TiO_5 single-phase nanoparticles, has better hydrophilic nature in comparison with both of TiO_2 nanoparticles and Fe_2O_3 nanoparticles [25].

In the present study, nanocomposite membranes based on (PBI)/strontium cerate nanoparticles were prepared and characterized. The prepared nanocomposite PBI based membranes containing SrCeO_3 nanoparticles showed higher acid uptake and proton conductivity.

2. Experimental

2.1. Materials

PBI with chemical structure of (poly(2,2'-*m*-(phenylene)-5,5'-bibenzimidazole), with a glass transition temperature of 425–435 °C, molecular weight (62000–59000 g mol^{-1}) was obtained from FumaTech corporation. Phosphoric acid (PA) and N, N-dimethylacetamide (DMAc) were purchased from Merck. Distilled deionised water (DI) was used through all experiments.

2.2. Synthesis of SrCeO_3 nanoparticles

Strontium cerate (SrCeO_3) nanoparticles were provided according to the literature procedure [26]. Initially, ammonium cerium (IV) nitrate ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$) and n-butanol ($\text{C}_4\text{H}_{10}\text{O}$) are reacted to synthesize cerium-n-butoxide ($\text{Ce}(\text{OBu})_4$). Ammonium nitrate (NH_4NO_3) can be removed from the solution including the synthesized cerium-n-butoxide. Next, the cerium-n-butoxide, strontium acetate ($\text{Sr}(\text{CH}_3\text{COO})_2$), and melted stearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_2$) were heated at 150 °C for 12 h to form a homogenous gel. The homogenous gel can be calcined at 1000 °C for 2 h. Finally, the strontium cerate nanoparticles with a particle size range of 21–32 nm were isolated.

2.3. Ion exchange capacity (IEC)

The ion exchange capacity (IEC) of PA-doped membranes was determined by the titration method. PA-doped membranes were soaked in a 2 M sodium chloride solutions for 24 h at RT to ensure replacement of H^+ groups with Na^+ groups. Subsequently, the solution was titrated with 0.1 M sodium hydroxide.

2.4. Preparation of PBI nanocomposite membranes

The PBI nanocomposite membranes were prepared by a solution-casting method. In this method, the nanocomposite membranes were fabricated using DMAc as a casting solvent. At room temperature, different weight percentages of nanoparticles with respect to the PBI (2, 4, 8, 12 and 16%), were dispersed in DMAc using an ultrasonic bath. Then, appropriate amounts of PBI powder was added to this solution under stirring at 120 °C. The obtained brown solution was cast onto a glass plate and the solvent was evaporated slowly at 120 °C for 5 h. The glass plates were then soaked in a de-ionized water bath. The membranes were slowly removed from the glass plates. Finally, the prepared membranes immersed in PA. PSC membranes are easily doped by PA.

PBI- SrCeO_3 nanocomposite membranes were named PSC. The value of x in PSC_x samples was assigned for the weight percent of the nanoparticles in the PBI membranes.

2.5. Acid uptake and leaching test

The resulting brown-colored PBI nanocomposite membranes were doped by immersion in aqueous PA (75 wt %) for 5 days. In order to separate the water content from the doping acid, the acid-doped membranes were dried at 110 °C under vacuum until the membrane weights were unchanged with time. The weight change in acid doping was measured and used for the calculation of acid doping level (acid molecule numbers per PBI repeating unit).

Leaching test is a method for the determination of PA retained by the PA-doped PSC_x membranes after washing with hot water (90 °C), which is considered one of the main degradation factors of this kind of membranes in the fuel cell. The PA-doped PSC_x membranes were immersed in de-ionized hot water for 2 h and then the remaining acid was obtained by a similar manner as described above.

2.6. FT-IR ATR spectra

The FT-IR ATR spectra (600–4000 cm^{-1} , resolution 4 cm^{-1}) were recorded with a Bruker Equinox 55 using an attenuated total reflectance (ATR, single reflection) accessory purged with ultra dry compressed air.

2.7. Proton conductivity measurements

The proton conductivity of membranes was calculated by the electrochemical impedance spectroscopy (EIS) with PGSTAT 303 N potentiostat/galvanostat (Ecochemie). The sample PA-PSC membrane was sealed between two platinum plates electrodes. The measurements were carried out on the potentiostatic mode. The spectra were recorded with signal amplitude of 50 mV in the frequency range of 100 Hz – 1 MHz with 100 points. The resistance of the membrane was obtained from the high-frequency intercept of the impedance. The conductivity values were calculated by using the equation ($\sigma = L/RS$), where, σ , L, R and S respectively refer to, proton conductivity, thickness, resistance from the impedance data and cross-sectional area of the membranes.

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