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Fabrication $BaZrO_3$/PBI-based nanocomposite as a new proton conducting membrane for high temperature proton exchange membrane fuel cells

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HIGHLIGHTS

- $BaZrO_3$ was used for the improving the proton conductivity of PBI.
- The high proton conductivity (125 mS/cm at 180 °C) was observed for the new PEM.
- Nanoparticles as protonic conductor can do as a special pathway for H^+ transport.
- The power density at 0.5 V and 180 °C was observed 0.56 W/cm^2.
- The membrane could be used as PEM for application in HT-PEMFC.

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ABSTRACT

Novel PBI (polybenzimidazole)-$BaZrO_3$ (PBZ) nanocomposite membranes have been prepared for the high temperature proton exchange membrane (HT-PEM) fuel cells. The results showed that the water uptake, acid doping level and proton conductivity of the PBZ nanocomposite membranes were higher than that of virgin PBI membrane due to the presence of perovskite structure $BaZrO_3$ nanoparticles, which as protonic conductor can perform as a special pathway for hydrogen transport. The proton conductivity of the PBZ nanocomposite membranes with 13 mol phosphoric acid per PBI repeat unit was obtained 125 mS/cm at 180 °C and 5% relative humidity. It was found that the performance of the fuel cells increases by increasing temperature; this was explained by faster reaction kinetic and higher proton conductivity. The power density and current density at 0.5 V 180 °C with 5% relative humidity were observed 0.56 W/cm^2 and 1.12 A/cm^2, respectively for PBZ nanocomposite membranes containing 4 wt% of the nanofillers. The results suggested that PBZ nanocomposite membranes are promising electrolytes for HT-PEM fuel cells with improved proton conductivity.

1. Introduction

Nafion is the most studied material as polymeric membrane in proton exchange membrane (PEM) fuel cells, because of its excellent chemical, mechanical, thermal stability and high proton conductivity in its hydrated state [1,2]. PEM fuel cells based on Nafion membrane have two main limitations. The first one is its high cost. The second is its dehydration at temperatures above 80 °C, causing an intense reduces in its proton conductivity and mechanical stability [3]. This also limits the working temperature below 80 °C, since the membrane dehydrates and the conductivity declines suddenly above this temperature. The improvement of high temperature PEM (HT-PEM) fuel cells is pursued universal in order to solve the problems of current cells based on Nafion [4].

The HT-PEM fuel cells suggestion many benefits compared with low temperature fuel cells. A common problem for low temperature fuel cells is cathode flooding caused by liquid water formed in the cathode [5]. This problem is not observed at higher temperatures due to existence of water vapor only. Hydrogen gas produced

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from hydrocarbons in a reformer will contain some CO. Fuel cell catalysts are very sensitive to CO. The adsorbed CO on the Pt catalyst surface hinders the favorite reaction. Catalyst poisoning with CO becomes much less pronounced in high temperature operations. In addition the higher temperature results in better heat distribution within a fuel cell stack, and a smaller and cheaper cooling system is required.

In the last decade, polybenzimidazole (PBI) membranes have been studied as membranes for PEM fuel cells. These membranes have very good properties that allow them to be used in HT-PEM fuel cells [6]. PBI-based fuel cells operated at temperatures above 185 °C can tolerate up to 3% CO [7]. The proton conductivity of virgin PBI is low, about 10^{-9} mS/cm [5,8]. However, its proton conductivity can be significantly increased by addition of different acids such as sulfuric acid, phosphoric acid (PA), perchloric acid, nitric acid or hydrochloric acid. Among these acids, PA is the most extensively used. PA has a high boiling point, high thermal stability, and high proton conductivity even in its anhydrous form. The proton conductivities of PA-doped PBI (PA-PBI) membranes have been widely considered [9]. One of the most promising membranes for operation above the boiling point of water is PA-PBI.

The proton conductivity of PA-PBI membranes increases with increasing doping level, temperature and humidification [10,11]. The influence of the humidification of PBI is much less than of Nafion membranes. However, an increase in relative humidity (RH) increases the proton conductivity for PA-PBI membranes, mainly at high temperatures. This can be described by interaction of water with excess PA [12]. A conductivity of 68 mS/cm at 200 °C and 5% RH was measured for PBI by He et al. [9]. This conductivity is close to the conductivity measured for Nafion membranes at 80 °C and 95% RH. For Nafion the electro-osmotic drag coefficient for water has been determined to vary between 0.9 and 3.2 at room temperature. For PA-PBI membranes, an electro-osmotic drag coefficient close to zero has been measured. This may show that a PA-PBI-based HT-PEM fuel cell can be operated without any humidification, although some humidification is beneficial.

The high proton conductivity is the highest challenges for commercialization and effective operation of PBI in HT-PEM fuel cells. The combine of extremely hydrophilic inorganic nanomaterial with a PBI creates favorable results, because of their affinity to intract with the water and acid and turn out to be more hydrophilic or more absorbent to water [13–17]. Incorporation of nanoscale additives to PA-PBI membranes concurrently increases the proton conductivity and mechanical stability of PA-PBI membranes, as well as growths their sustainability in fabrication of membrane electrode assembly (MEA). The addition of sulfonated silica nanoparticles to PBI can successfully increase the proton conductivity and advance the mechanical strength of the resulting membranes [18].

The perovskite-type oxides are known as high temperature proton conductors, which are promising materials for fuel cells. In general, protonic conductors with perovskite structure have concerned plentiful consideration over the last few years due to their high chemical stability, excellent thermal and mechanical stability, relatively low cost and high applicability in electrochemical devices for energy generation [19]. Therefore, the study and understanding of their proton transport properties is of numerous attention and important to extend the capabilities of application in an industrial scale method [20].

$BaZrO_3$ with considerable levels of protonic conductivity [21,22] has an enormous potential for use in fuel cells [19]. $BaZrO_3$ has concerned much consideration for its applications in PEM fuel cells such as: simple cubic perovskite structure, excellent mechanical and structural integrity under extreme thermal excursions [23] and high chemical stability. $BaZrO_3$ is the best proton conductors with perovskite structure and exhibit small activation energies for proton migration.

The term perovskite presently is generally employed to name a particular group of oxides with common formula ABO_3. A perovskite-type oxide is structurally stable due to its well-balanced geometrical arrangement of basic atoms and their valences [19]. Perovskites can be synthesized with a widespread variation of array of chemical elements, because cations of large (site A) and small (site B) ionic radius are well suitable in the crystalline structure. The A-site can be occupied by cations M^{+} (Na, K), M^{2+} (Ca, Sr, Ba) or M^{3+} (Fe, La, Gd) and B-site can be occupied either by M^{5+} (Nb, W), M^{4+} (Ce, Zr, Ti) or M^{3+} (Mn, Fe, Co, Ga) [20]. In many perovskites, the proton conductivity is highly adequate to be developed in different applications, such as fuel cells [24]. Perovskites are predominantly proton conductors at high temperatures.

In previous studies, we introduced new proton conducting hybrid membranes for PEM fuel cells based on poly(vinyl alcohol) and nanoporous silica containing phenyl or propyl sulfonic acid [25,26] and poly(vinyl alcohol) and poly(sulfonic acid)-grafted silica nanoparticles [27,28]. Newly, Nafion nanocomposite membranes based on Fe_2TiO_5 perovskite were prepared by dispersion of Fe_2TiO_5 nanoparticles within the commercial Nafion membranes [29]. Incorporation of Fe_2TiO_5 nanoparticles in Nafion matrix improved the thermal stability of Nafion membranes which is important for HT-PEM fuel cells. As we mentioned it seems that in Fe_2TiO_5 nanoparticles when Fe^{3+} cations are placed near Ti^{4+} cations, the acidic character of these ions will increase.

In the present work, special attention was paid to the influence of the $BaZrO_3$ nanoparticles on the proton conductivity and fuel cell performance of PBI-$BaZrO_3$ nanocomposite membranes for application in HT-PEM fuel cells. As a result, PBI-$BaZrO_3$ nanocomposite membranes have exhibited improved proton conductivities and high single cell performance compared to the virgin PBI membrane.

2. Experimental

2.1. Materials

Polybenzimidazolewas obtained from Fumatech. PA and N,N-dimethylacetamide (DMAc) were purchased from Merck. LiCl was purchased from Aldrich. Distilled de-ionized was used through all experiments.

2.2. Synthesis of $BaZrO_3$ nanoparticles

$BaZrO_3$ nanoparticles with a particle size range of 20–25 nm were prepared according to the literature procedure [30]: An appropriate amount of stearic acid was first melted in a beaker at 73 °C. Subsequently, barium stearate was added. After that, stoichiometric tetrabutyl zirconate was added to the resulted green transparent solution and stirred to form a homogenous light sol. Then the sol naturally cooled down to room temperature, and dried in an oven for 12 h to obtain dried gel. The prepared gel was calcined in air to obtain nano-crystallites of $BaZrO_3$.

2.3. Preparations and characterizations of PBI nanocomposite membranes

2.3.1. Preparation of membranes

The PBI nanocomposite membranes were prepared by a solution-casting method. In this method, PBI/LiCl/DMAc (2 wt%) solution was prepared by dissolving PBI/LiCl (1:1) in DMAc under a nitrogen atmosphere at 150 °C. At room temperature, different weight percentages of nanoparticles were dispersed in above viscous brown solution using an ultrasonic bath. The solution was