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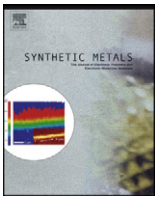

Poly(vinyl alcohol)-colloidal silica composite membranes for fuel cells

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ABSTRACT

The aim of this study is to develop an environmentally and friendly poly(vinyl alcohol) based low cost membrane with improved ionic conductivity, thermal and mechanical stability. In this work, the effect of colloidal silica content on membrane properties was investigated. Sulfosuccinic acid (SSA) was used as the sulfonating agent. In order to enhance the mechanical and ionic conduction properties, colloidal silica was used. The range of silica content in the membrane solution investigated was 5–20%. For the characterizations, the synthesized membranes were subjected to FT-IR, TGA, tensile strength analysis, water uptake, ion exchange capacity (IEC) and impedance measurements for proton conductivity. Synthesized membranes demonstrated high water uptake (up to 80%) without swelling, high ion exchange capacities was found to increase with increasing SSA content. The proton conductivity of CS doped membranes increased with increase in temperature and the temperature dependence showed significant change in the CS doped membranes. An increase in the values of the proton conductivity was driven by the mobility of free charges (free ions) as the temperature was increased. Addition of SSA and CS to the polymer matrix improved the thermal stability of the membranes. It was also discovered that membranes were in a composite structure and colloidal silica particles did not contribute to the structure of the polymer matrix at the molecular level. Mechanical durability of the membranes having SSA content above 15% decreased and these membranes showed a more fragile structure.

1. Introduction

Proton Exchange Membrane Fuel Cells (PEMFCs) are among the most promising power sources due to their high efficiency, high power density, environmentally friendly technology, flexible operation and their adaptability for both mobile and stationary applications [1–4]. Unfortunately there are certain problems in their commercialization. Foremost is the lack of a suitable and low cost membrane with high proton conductivity, high chemical stability and mechanical strength. Membranes, which are regarded as the hearts of the PEMFCs and perfloro sulfonated membranes, such as Nafion are widely used. However, due to their high cost, loss in proton conductivity at high temperatures and methanol loss of over 40% in DMFCs, the search for the development of cheaper alternatives with high proton conductivity, lower methanol crossover and higher chemical and mechanical stability is an on-going effort [5,6]. Various materials have been investigated for preparing proton exchange membranes (PEM) and results are summarized in recent reviews [7,8].

Among the materials investigated, poly(vinyl alcohol) (PVA) is on the forefront due to its good mechanical properties, chemical stability, low cost, film forming ability, high hydrophilic behavior [9–11]. Although PVA based membranes suffer from their solubility in water and PVA itself does not have fixed charges, these problems can be overcome. For example, cross linking with a multifunctional compound by using one of the reported cross linking methods may be used to decrease the solubility of membranes [12,13]. As a rule, all multifunctional compounds are capable of reacting with the hydroxyl group; for example, aldehydes react with PVA to form acetal or hemiacetal linkages. Another approach for rendering PVA insoluble may be modification with organic or inorganic additives or organic–inorganic hybridization [14–17]. Hybrid organic–inorganic composites have been the subject of a large number of studies because of their easily controlled physical properties through the combination of organic polymer matrix with inorganic compounds [18–20]. It was suggested by Kim et al. [21] that in these organic–inorganic hybrids, inorganic minerals precipitate in situ in a regular manner in the organic polymer matrix and a strong interaction between the organic polymer and inorganic mineral results in a hybrid with markedly improved mechanical properties. Another important disadvantage of PVA as a membrane material is its swelling. Swelling reduces the mechanical strength of the membrane and is especially detrimental for DMFCs since it increases the methanol cross-over. Swelling can be controlled and limited by partial cross linking [22]. Thermal treatment [23] or some cross linking agents such as glutaraldehyde [24] or maleic acid [25] can be used for this purpose.

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Some fillers have also been used to increase proton conductivity and mechanical stability of PVA based membranes. Depending on the nature of these fillers, organic–inorganic hybrid membranes exhibit different properties. For example, tetraethyl orthosilicate (TEOS) provides a dense inorganic structure with a high degree of cross linking for increasing both thermal and chemical stabilities [26]. In another study, it was shown that addition of large amount of functionalized phosphorous groups to the composite membrane allows for protons hopping to dominate proton conduction while diffusion transport of protonic ions is favoured by the polymeric matrix [27]. In these studies one of the frequently encountered problems are the difficulties related to the incorporation of hydrophilic oxides (e.g. SiO_2). These oxides are too large to enter the pore structure of the membrane [28]. A sol–gel technique is suggested for the solution of this problem by Mauritz [29]. In his study, Mauritz has shown that oxides can enter the finer channels (~5 nm).

Although in most PVA based hybrid membranes TEOS has been used as a silica source [14,30,31], we attempted to develop a cross-linked PVA based composite membrane in which CS was used as the silica source. An improvement in mechanical properties due to cross linking with sulfosuccinic acid (SSA) as well as an increase in proton conductivity due to the addition of sulfonic acid was expected to be achieved.

2. Experimental

2.1. Materials

In this study, poly(vinyl alcohol) (99% hydrolyzed, average Mwt = 145,000, Sigma–Aldrich) and sulfosuccinic acid (SSA) (70 wt% aqueous solution, Sigma–Aldrich) were used as the backbone polymer matrix and the cross linking agent respectively. Colloidal silica (Ludox AS-40, 40 wt% ammonium stabilized colloidal silica solution in water, Aldrich) was used as the inorganic filler. In all experiments deionized water was used unless otherwise stated.

2.2. Membrane preparation

5 wt% PVA solution was prepared and made to undergo 6 h of continuous stirring at 90 °C. SSA was added to this in proportions varying from 5% to 20% at 50 °C and then CS was added in varying proportions (from 5% to 20%) and mixed at room temperature for 4 h. The homogeneous mixture thus obtained was poured onto a polyethylene plate and allowed to be dried for 1 week. The dry membranes were peeled from the plate and subjected to thermal treatment for 1 h at 125 °C. Membrane thickness was measured with probe using magnetic induction principle. Measurements were carried out with a Sheen–Eco Test Plus coating thickness gauge. For each sample, at least 20 measurements were made at different regions and average membrane thickness of $120 \pm 8\ \mu m$ was obtained. The membranes were stored in deionized water after pretreatment in order to ensure equilibration prior to use in conductivity measurements.

2.3. Membrane characterization

FT-IR measurements of the prepared membranes were performed with a Jasco FT/IR-480 Plus Spectrometer (Jasco Inc. Analytical Instruments, Japan) operating in the wave number range of 400–4000 cm^{-1}. The degradation process and the thermal stability of the membranes were investigated using thermogravimetry (TGA) (Setaram Instruments, Setsys Evolution model). The TGA measurements were carried out under nitrogen atmosphere using a heating rate of 10 °C/min from 50 °C to 500 °C.

Mechanical strength of the membranes was measured by AG-I 5 kN (Shimadzu AutoGraph, Japan) testing machine with an operating head load of 0.25 kN. Cross-sectional area of the samples of known width and length were calculated. The membranes were then placed between the wave shaped grips of the testing machine. The grip length was 2 cm and the speed of testing was set to 4 mm/min. Tensile strength of the membrane was calculated using the following equation [36]:

$$\text{tensile strength}\,(\text{N/mm}^2) = \frac{\text{max load}\,(\text{N})}{\text{cross-sectional area}\,(\text{mm}^2)} \quad (1)$$

Solartron 1260 Impedance Gain/Phase Analyzer (IGPA) and 1287 Electrochemical Interface (EI) combination was used by means of two-probe technique for proton conductivity. At least three specimens were tested for each composition and then averaged.

2.4. Water uptake and ion exchange capacity (IEC)

The water uptake of the membrane was determined by measuring the change in weight before and after hydration. The membrane was immersed in deionized water for 24 h. The wetted membrane weight (W_{wet}) was then measured as soon as the surface-attached water on the membrane was removed with filter paper. The weight of the dry membrane (W_{dry}) was determined after drying it in a vacuum at 60 °C for 1 day. The water uptake (%) was calculated using the following equation [6,38]:

$$\text{water uptake}\,(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (2)$$

Ion exchange capacities (IECs) of the samples were estimated by a titration method using a computer controlled Shott Alpha Plus Model TA-50 system with 0.01 mL sensitivity. The ion exchange capacity was calculated using the following equation [6]:

$$\text{IEC} = \frac{M_{i,\text{NaOH}} - M_{f,\text{NaOH}}}{W_{\text{dry}}} = \frac{H^{+}(\text{mmol})}{W_{\text{dry}}} \quad (3)$$

where $M_{i,\text{NaOH}}$ is the initial mmol of NaOH used for titration and $M_{f,\text{NaOH}}$ is the mmol (meq) of NaOH after equilibrium. H^+ is the molar number of proton sites presented in the membrane, and W_{dry} is the weight (g) of the dry membrane.

2.5. Proton conductivity

The most important property of a fuel cell membrane is its proton conductivity which determines the cell efficiency to a great extent. A specially designed home made cell was used for measuring proton conductivity. To measure it, two stainless steel blocking electrodes with active surface areas of 1.4 cm^2 were used. Before the measurement, samples were soaked in deionized water for 24 h and the membranes were sandwiched between the electrodes in temperature controlled humidity chamber.

A teflon sheath was used to insulate the stainless steel electrodes and also to force the current to pass through the membrane. The pressure necessary to maintain a good contact between the electrodes and the membrane was provided using a spring attached to one of the electrodes.

In order to reduce the surface contact resistances and to keep the electrode surfaces clean, flushing and vigorous polishing were applied. This sample holder was used together with a Solartron Instruments (1260+1287). Although the four-probe technique [40] is commonly used to measure the membrane proton conductivity, in this study, the impedance measurements were carried out using the two-probe technique by applying ac stimulus current between the frequencies of 1 Hz–10 MHz with 10 mV. The pro-