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# Nanocomposite proton exchange membranes based on Nafion containing $Fe_2TiO_5$ nanoparticles in water and alcohol environments for PEMFC

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ABSTRACT

In this study, the preparation and characterization of Nafion/$Fe_2TiO_5$ nanocomposite membranes for proton exchange membrane fuel cells (PEMFCs) were investigated. Nafion/$Fe_2TiO_5$ nanocomposite membranes were prepared by dispersion of $Fe_2TiO_5$ nanoparticles within the pure commercial Nafion membranes. The composition percentage of the nanocomposite membranes and the solvent used for the dispersion of nanoparticles within the membranes were varied in order to study the effect of these variations on the proton conductivity, water uptake and also the thermal stability of the membranes. The nanocomposites membranes were characterized by using thermogravimetric analysis (TGA), scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) spectroscopy and impedance spectroscopy (IS). The prepared $Fe_2TiO_5$ nanocomposite membranes showed a higher water uptake, proton conductivity and thermal stability compared with the pure commercial Nafion membranes. The highest proton conductivity (226 mS/cm) was observed for the membranes containing 2 wt% of $Fe_2TiO_5$ nanoparticles and prepared in de-ionized water (DI) as solvent.

## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) display the highest power densities compared to the other type of fuel cell [1]. Polyperfluorosulfonic acid (PFSA) membranes, such as Nafion, are the most common type of polymeric membranes used for PEMFC due to their excellent chemical, mechanical, thermal stability and high proton conductivity in their hydrated state [2] But, one great drawback of Nafion membranes is their dehydration at temperatures above 80 °C, causing a dramatic decrease in their proton conductivity and mechanical stability [3]. Significant efforts have been made to modify Nafion membranes for application at low humidity or elevated high temperatures [4,5]. Studies have shown that the addition of hygroscopic metal oxide nanoparticles such as $SiO_2$, $ZrO_2$, and $TiO_2$ to Nafion can improve the water uptake, proton conductivity, thermal stability and fuel cell performance of PEMFC prepared based on Nafion at higher temperatures [6,7]. The hygroscopic characteristics of these nanomaterials cause a greater extent of absorption of water molecules in the Nafion membrane [8]. Compared to the conventional micron-sized particles, nanoparticles have a much higher surface-to-volume ratio. As the particle size decreases, the percentage of molecules/atoms present on the surface is increased tremendously [9]. It is believed that the proton transfer takes place on the surface of these nanoparticles and their high surface area improves the surface chemistry [10,11]. The sol–gel and solution casting methods mostly have been applied for impregnation of the proton exchange membranes with desired nanoparticles [12]. Depending on the nature and the polarity of the solvent used during these methods, the penetration rate and percentage of nanoparticles through the membranes will differ. Recently, we introduced new proton conducting hybrid membranes based on polyvinyl alcohol, PVA, and nanoporous silica containing phenyl sulfonic acid [13] and poly(sulfonic acid)-grafted silica nanoparticles [14] for PEM fuel cells.

It is known that the penetration of different solvents into Nafion membrane has different proton conductivity effects in this polymer [15]. It is likely that variation of solvents causes the nanoparticles to be directed to different parts of the membrane. Investigating the effect of the solvent polarity on the structure of Nafion membrane has shown that depending on the polarities of the solvents, Nafion can undergo both micro- and macrostructural deformations [16]. $TiO_2$ is a good hydrophilic filler candidate for the PEMFCs, because it allows a suitable hydration of the

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membrane to be maintained under fuel cell operating conditions [17]. The addition of $TiO_2$ nanoparticles into a Nafion membrane has been reported [18] as an effective method to enhance the water retention ability of Nafion membrane. Zhao et al. reported enhanced water uptake and proton conductivity for Nafion–$Fe_2O_3$–$SO_4^{2-}$ nanocomposite membranes, which were prepared by a solution casting method [19].

The –OH groups of $Fe_2TiO_5$ nanoparticles, as mixed metal oxides, provide strong hydrogen bonding sites and increase the contents of the bound to free water ratio into the membrane matrix. Also, nanoparticles possess a negative surface potential that are influenced by surface groups [20]. The main cations in $Fe_2TiO_5$ nanoparticles are $Ti^{4+}$, $Fe^{3+}$ [21]. According to the Lewis acid–base theory, the former two are classified as hard acids. This means that the following polar groups will react with –OH groups of water. $TiO_2$ nanoparticles only have $Ti^{4+}$ cations. It seems that when $Fe^{3+}$ cations are placed near $Ti^{4+}$ cations in the $Fe_2TiO_5$ structure, it results in intensification of acidic effect and makes strong bonds with –OH groups of water. Hence, $Fe_2TiO_5$ nanoparticles with provision of strong acid sites have good hydrophilic nature compared with $TiO_2$ nanoparticles.

In the present work, Nafion/$Fe_2TiO_5$ nanocomposite membranes were prepared by dispersion of $Fe_2TiO_5$ nanoparticles within the commercial Nafion membranes. The composition percentage of the nanocomposite membranes and the solvent used impregnation of the membranes were varied in order to study the effect of these variations on the proton conductivity, water uptake, thermal stability and also the morphology of the membranes. For investigation of nanoparticles penetration into Nafion membrane we have changed the solvent polarity from aqueous environments to pure alcoholic environments. The percentages of nanoparticles in the membranes were optimized for maximum water uptake and proton conductivity.

## 2. Experimental

### 2.1. Materials

DuPont Nafion with an equivalent weight of 1100 was purchased from Aldrich in the form of a sheet of Nafion-117 perfluorinated membrane with a thickness of 0.007 in. (0.2 mm) in acid form. Ethanol (96%) was purchased from Merck and used as received. Distilled de-ionized water (DI) was used through all experiments.

### 2.2. Synthesis of $Fe_2TiO_5$ nanoparticles

$Fe_2TiO_5$ nanoparticles were prepared according to the literature procedure [22]: iron acetyl acetonate, tetra-n-butyl titanate and stearic acid were all of analytical grade reagents. First, an appropriate amount of stearic acid was melted in a beaker at 73 °C. Subsequently, a fixed amount of iron acetyl acetonate was added to the melted stearic acid and then dissolved to form a transparent brown solution. After that, stoichiometric tetrabutyl titanate was added to the solution and stirred to form a homogeneous light brown sol. It was then naturally cooled down to room temperature and dried in an oven for 12 h to obtain dried gel. Finally, the gel was calcined at 700 °C, 800 °C, and 900 °C temperatures in air to obtain nano-crystallites of $Fe_2TiO_5$ in particle size range of 48–70 nm.

### 2.3. Pre-treatment of Nafion membranes

In order to enhance the penetration rate of nanoparticles into the polymer, the Nafion membrane (in acid form) was roughened gradually at both surfaces using a fine silicon carbide abrasive paper [23]. In order to remove all impurities introduced into the polymer during the manufacturing process, the roughened membranes were decontaminated through an extensive cleaning procedure, suggested by MacMillan and colleagues [24,25]. The cleaned Nafion membranes were then stored in distilled deionized water to be kept hydrated for future applications.

### 2.4. Preparation of Nafion/$Fe_2TiO_5$ nanocomposite membranes

At room temperature, different weight percentages of $Fe_2TiO_5$ nanoparticles were dispersed in water, ethanol and water/ethanol (1:1 v/v) mixture, using an ultrasonic bath. The pre-treated hydrated Nafion membranes were immersed in the dispersed solutions of $Fe_2TiO_5$ nanoparticles and left for 24 h while stirring. The samples prepared in water-, ethanol- and water/ethanol (1:1 v/v) mixture-based dispersed solution were named NH, NE and NHE, respectively. The value of $x$ in NH-$x$, NHE-$x$ and NE-$x$ samples was assigned for the wt/wt percent of the nanoparticles vs. Nafion membrane in 10 mL solvent.

The exact amount of nanoparticles incorporated into the nanocomposite membranes was calculated from Eq. (1).

$$NP\,\% = \frac{NP_p - NP_f}{W_M} 100 \tag{1}$$

where, $NP_p$ and $NP_f$ are weights of the primary and final (after nanocomposite preparation) $Fe_2TiO_5$ nanaoparticles in the solvent, respectively. $W_M$ is weight of the Nafion membrane.

### 2.5. Water uptake measurements of nanoparticles

The water uptake of the nanoparticles was calculated by the following Eq. (2):

$$WU = \frac{W_{NP/wet} - W_{NP/dry}}{W_{NP/dry}} 100 \tag{2}$$

where, $W_{NP/wet}$ and $W_{NP/dry}$ are weights of the wet and dry nanoparticles, respectively. To the wet weight of the nanoparticles, a certain amount of nanoparticles was put into a test tube in 100% RH for 24 h. The fully hydrated nanoparticles were then removed from test tube and weighed instantly. To obtain the dry weight of the nanoparticles, they were placed in an oven at 80 °C for 24 h, and then weighed immediately. The same procedure was repeated three times and the mean was used.

### 2.6. Water uptake measurements of membranes

The water uptake of the prepared membrane samples was calculated from Eq. (3).

$$WU_M = \frac{W_{M/\mathrm{wet}} - W_{M/\mathrm{dry}}}{W_{M/\mathrm{dry}}} 100 \tag{3}$$

where, $W_{M/wet}$ and $W_{M/dry}$ are weights of the wet and dry membranes, respectively. To determine wet weight of the samples, they were equilibrated in distilled deionized water at room temperature for 24 h. The fully hydrated samples were then removed from water and their surface was gently dried by a soft tissue paper and weighed instantly. To obtain the dry weight of the samples, they were placed in an oven at 80 °C for 24 h, and then weighted immediately. The same procedure was repeated four times and the mean was used.

### 2.7. Proton conductivity measurements

The proton conductivity of membrane was measured by a three-electrode method using AC impedance spectroscopy with