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The development of Speek/Pva/Teos blend membrane for proton exchange membrane fuel cells

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A B S T R A C T

Sulfonated poly ether ether ketone (SPEEK) has high potential for proton exchange membrane fuel cell (PEMFC) application and has been widely considered as most promising alternative to commercial membranes. In this study a novel ternary composite membrane consisting of SPEEK/poly (vinyl alcohol) (PVA) and tetraethyl ortosilicate (TEOS) were prepared by blending and casting method. The obtained samples were characterized by FT-IR, dynamic mechanical analysis (DMA), electrochemical impedance spectroscopy (EIS), oxidative and hydrolytic stability, water uptake capacity, swelling property and ion exchange capacity tests. According to these characterization test results, the addition of PVA in the membrane structure increased the mechanical strength and in addition TEOS is easily incorporated into the membrane structure because of the presence of modifiable groups in PVA. The addition of TEOS to blend membranes prevented water loss at high temperatures and TEOS addition indirectly increased the proton conductivity of the membranes. The highest performance of 600 mA/cm^2 was obtained SP90/PV10/TE coded membrane at 0.6 V cell potential and fuel cell operate at 1 atm and 80 °C. At the same conditions Nafion 117 gave 400 mA/cm^2. This study shows that blend membrane seems to be a promising alternative membrane for PEMFC application.

1. Introduction

Fuel cells are considered to be one of the best energy conversion systems because of their advantages such as low environmental pollution, efficient power generation, quick start up and safe operation [1,2]. Among all the other types of fuel cells, proton exchange membrane fuel cells (PEMFCs) are one of the best promising alternatives and extensively studied because of the several advantages including eco-friendliness, low operating temperature, high efficiency, high power density and low weight [3–6]. The most important component of the PEMFCs is the proton exchange membrane (PEM). Perfluorinated sulfonic acid membranes (PFSA) are widely used as commercial PEMs because of their high proton conductivity, electrochemical stability and high mechanical strength [7–9]. However, problems of performance loss and dehydration occurs at high temperature, high fuel cross over and their high cost [10,11]. Therefore recent researches have focused on the development of alternative membranes which have high proton conductivity, good electrochemical and mechanical stability and low cost. Poly benzimidazole (PBI) [12,13], poly ether sulfone (PES) [14,15], polyvinyl alcohol (PVA) [16,17], poly ether ether ketone (PEEK) [18–20], polyphenyl sulfone (PPSU) [21], poly sulfone [22] etc. are used as main chain of PEM and among these hydrocarbon polymer PEEK is the most investigated and studied because of PEEK has such properties that low cost, eco-friendly, high thermal, mechanical and chemical stability, simple preparation process and improvable proton conductivity via post sulfonation [22–29]. Sulfonated PEEK (SPEEK) can be obtained by sulfonation of PEEK. Properties of synthesized composite membrane related to the degree of sulfonation therefore sulfonation should be controlled [18,30,31].

Studies at different sulfonation degrees have been carried out in the literature [18,32]. The sulfonic acid groups separate the protons from each other by water molecules and provide proton transport. The number of acidic groups increases with the degree of the sulfonation membranes is increased. According to studies, membrane properties have increased to a certain degree of sulfonation. After a certain degree of sulfonation, the mechanical strength properties of the membranes are reduced and swell significantly at high temperature and humidity [18].

Researchers are being conducted to increase the mechanical

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strength and swelling properties of SPEEK membranes at high degree of sulfonation. For this reason, additives such as heteropoly acids [33,34], natural zeolytes [18] and boron phosphate [16] are added to the membrane matrix to increase the membrane properties. Hydrophilic additives are added to the structure to improve the self-humidifying property under high temperature and low humidity conditions [35–37].

In hybrid membrane studies, membrane properties were tried to be increased by using SiO_2 [38–42]. SiO_2, one of the inorganic additives, is widely used in synthesis of composite membranes. SiO_2 has hydrophilic property which is able to uptake water more strongly. Water molecules are strongly hydrogen bonded to the ions in the inorganic materials [43].

In studies conducted with TEOS, it has been shown that the water uptake capacities of the synthesized membranes increase even at high temperature and low relative humidity due to the presence of TEOS additive.

In some studies where TEOS is used as the SiO_2 source for the membrane structure TEOS converted into silica by hydrolysis in acidic medium and then doped to the composite membrane [45]. Apart from TEOS, polydimethoxysiloxane (PDMOS), mercaptopropyltriethoxysilane (MPTES) [46] as a source of SiO_2 can be directly incorporated into the membrane. SiO_2 powder can also add to the membrane [47]. Since the distribution of the powder contribution in the solution is not efficient and TEOS is widespread in the literature studies [48,49], the use of TEOS as the SiO_2 precursor is aimed in this study.

Recently, in order to improve the membrane properties, the hybrid membranes comprising inorganic phase incorporated with polymer matrix have been widely investigated [1,50–53]. It was seen that the mechanical properties of the membrane did not increase much, although the proton conductivity value increased as the amount of SiO_2 increased. PVA is used as an alternative membrane because it has high hydrophilic character and can be easily modified. PVA widely used as a polymer matrix in blended membranes because of its good film forming ability, hydrophilic nature, chemical and mechanical properties. PVA can be easily modified due to its OH- groups in its structure. The polyvinyl alcohol provides significant increase in thermal and mechanical strength values due to its efficient cross-linking with aldehydes [54–58].

In this study, it is aimed to develop an alternative composite membrane to commercial PFSA membranes. SPEEK polymer, which has high proton conductivity at high sulfonation degree, high thermal and chemical stability, constitutes the main chain of the membrane. A blend membrane was synthesized with PVA and SPEEK in order not to lose the mechanical and chemical properties of the membrane at medium sulfonation degree of PEEK. In the same way, SiO_2 containing TEOS is added to the membrane matrix in order to not lose the moisture property of the membrane at high temperature and low humidity conditions. Membranes were synthesized by using classical sol gel method and their characterization experiments such as FT-IR analysis, water uptake capacities, swelling ratio, ion exchange capacity, proton conductivity, mechanical strength, oxidative and hydrolytic stability tests were carried out. Also their fuel cell performance parameters were determined in a fuel cell test station.

2. Materials and methods

2.1. Materials

Membrane structure was made of PEEK polymer as pellets (polyoxy-1,4-pheneyleneoxy-1,4-pheneylene carbonyl-1,4-phenylene, Aldrich, Mw: 20,800), PVA (polyvinyl alcohol %99, Aldrich, Mw: 124,000) and TEOS (tetraethyl ortosilicate, %50, Merck). Concentrate sulfuric acid (Aldrich, % 99.8) were used as active group. N, N dimethylacetamide (DMAC, Aldrich, %99.8) was used to solve SPEEK. Carbon cloth (Ion power) was selected as gas diffusion electrode. The Nafion 117 membrane from Dupont was used for comparison to commercial products. Pt/C (%20 Pt VULCAN XC72) and isopropyl alcohol (>97.5) were purchased from Fuel cell store. All chemicals used in high purity without using any purification steps.

2.2. Sulfonation of PEEK

PEEK pellets were dried in vacuum oven at 100 °C prior to sulfonation progress. The PEEK pellets were mixed in concentrated sulfuric acid at constant temperature. The sulfonation process was continued until the sulfonation degree reached a certain value. The solution was poured into ice to terminate the reaction. Then SPEEK polymer strings were washed with deionized water. The washing process was repeated until the neutralization occurred. After neutralization, the polymer strings were dried in vacuum oven at 50 °C.

2.3. Preparation of blend membranes

SPEEK/PVA in a different mass ratio (90:10, 70:30, 50:50) and 10% SiO_2 doped membranes coded as SP90/PV10/TE, SP70/PV30/TE, SP50/PV50/TE, SPEEK/PVA in a different mass ratio 90:10 membrane (SP90/PV10), pure SPEEK and pure PVA membranes were synthesized for parametrical study. Many studies in the literature are carried out at a certain amount of additives and the effect of this additive on the membrane properties is examined [21,44,59,60]. The membrane properties increase up to a certain ratio then the properties of the inorganic additive come to the forefront and the membrane properties are decreases [16,43,61,62]. Here the additive is more like a supporting material. Since this ratio is 10–15% in the literature, this study was carried out as 10% SiO_2. Firstly, 5% aqueous solution of PVA was prepared. SPEEK strips obtained after sulfonation were dissolved in DMAc at 50 °C. SPEEK and PVA solutions were mixed in a magnetic stirrer. After mixing two mixtures in the membrane synthesis stage, the temperature was increased to 80 °C and stirring was continued for 12 h under the viscosity control. Evaporation of large amount of the water, which is one of the polar solvents, is provided. Acidic catalyzed reaction of TEOS in aqueous medium was performed as follows [48].

$$Si(OC_2H_5)_4 + H_2O \xrightarrow{\text{acid catalyst}} Si(OH) + C_2H_5OH$$

The Si(OH) containing aqueous solution is mixed at a certain ratio. Bandelin Sonopuls brand Ultrasonic homogenizer was used for homogenous distribution. Ultrasound was applied at 40% amplitude for 30 min. After homogenous solution was obtained, membranes were poured into petri glass with drop casting method. Membranes were dried in a vacuum oven at 50 °C for 4 days in order to avoid bubbling and composite membrane synthesis is completed. In order to enhance the mechanical properties of composite matrix thermal crosslinking process were applied at 130 °C. Synthesized membranes were subjected to protonization before characterization tests.

2.4. Preparation of catalyst ink and MEA fabrication

Membrane electrode assemblies (MEA) were prepared for single cell performance tests. Solution containing %10 Pt on VULCAN XC-72, 5% Nafion solution and 7/1 isopropanol/distilled water were prepared and mixed at ultrasonic homogenizer at 40% amplitude for 2 h. Catalyst ink was sprayed onto composite membranes until the desire Pt loading was achieved. Gas diffusion layers were placed