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Functionalized poly(vinylidene fluoride-co-hexafluoro propylene) membrane for fuel cell

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HIGHLIGHTS

- Functionalization of fluoropolymer has been done to design membrane for fuel cell.
- Membrane efficiency in terms of power density, and methanol permeability is found superior.
- Thermal and mechanical stability of the membrane boost it real application in fuel cell membrane.
- Reason for superior behaviour is revealed from functionalization point of view.

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ABSTRACT

Functionalization of poly(vinylidene fluoride-co-hexafluoro propylene) (HFP) is made to prepared membrane for its application in fuel cell. The sulphonation of HFP membrane is carried out under control condition to maintain its stiffness and toughness of the membrane. The evidence of functionalization (sulphonation) is confirmed through different spectroscopic techniques such as NMR, FTIR, EDS mapping and UV–visible measurement and the degree of sulphonation is calculated from the integral peak area. The structural change from the usually crystallized α-phase to piezoelectric γ-phase in functionalized membrane is established through XRD studies. Mechanical and thermal stabilities of the membrane are established through universal testing machine and thermogravimetric measurements. Suitability of proton exchange membrane has been verified through their high water uptake (12%), low fuel permeability (4.43×10^{-7} cm^2 s^{-1}) and thermal stability (up to 200 °C). The proton conductivity is found to be high in functionalized membrane while its low fuel permeability and high temperature stability is very good as compared to standard Nafion membrane. Efficiency of the membrane is reported in the form of selective parameter (ratio of conductivity and methanol permeability) of value 0.78×10^5 S cm^{-3}.s for functionalized HFP against the value of 0.81×10^5 S cm^{-3}.s for standard Nafion 117. Moderately high open circuit voltage (0.63 V) and power density of 48.34 mW/cm^2 is reported indicating very good performance of the overall membrane for direct methanol fuel cell. Therefore, direct functionalization of a polymer is a better approach for the preparation of fuel cell membrane.

1. Introduction

The real problems of the twenty first century are the energy resources as the conventional resources of energy such as coal, natural gas and petroleum are exhausting very fast. Conventional energy resources also increase the environmental pollution resulting global warming which affects the animal life including human [1–4]. To solve these energy problems with its high demand, much efforts are required to move towards nonconventional energy sources and stationary portable power sources like solar cell, wind energy, redox flow battery, fuel cell etc. [5–7]. In this context, the polymer electrolyte membrane fuel cells (PEMFC's) play an important role in future energy demand as it provides clean energy, environmental friendly, and efficient power source [8–10]. Although polymeric membrane has many other applications such as filtrations techniques; ultrafiltration, microfiltration, nanofiltration, reverse osmosis, adhesive, water distillation by electro-dialysis

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(ED), production of salt from seawater, radionuclide's transporter and proton exchange membrane [11–14]. Amongst them, proton exchange membrane is one of the major applications which is useful in fuel cell technology as an electrolyte cum separator and allows proton to pass through the membrane [15,16]. The membrane for PEMFC should have the desired properties like high ionic conductivity, low fuel permeability, thermally and mechanically stable in operating conditions, low cost, sufficient water uptake of membrane and better fuel cell performance [17–19]. Nafion 117 membrane is widely used for different purposes but has many disadvantages such fuel crossover, low operating temperature and cost of the membrane [20]. In the present scenario, several scientists have explored the advanced functionalized membranes to replace the Nafion using several technologies such as graft copolymerization, direct functionalization, high energy swift heavy ions bombardment followed by functionalization, block copolymerization methods etc. to minimize the cost, ease of processing along with greater temperature window for operation [21–23]. Now, the significant progress has been made to achieve the challenges and worldwide use of the target materials in PEMFC, mainly in portable power generation including automobiles industry [24]. The polymer membranes in PEMFC technology use functionalized membranes with different functionalities such as sulphonate group, phosphates group, chloride, nitrite, quaternary ammonium salt, quaternary phosphonium salt etc. to achieve high ionic conductance of the membranes [25,26]. Fluoropolymers like poly(vinylidene fluoride) (PVDF) and its copolymers are nonreactive, insulating, mechanically tough, thermally and electrochemically stable. Fluoropolymers are the most encouraging polymer as compared to Nafion 117 for fuel cell membrane application [27,28]. Fluoropolymer (PVDF) and its copolymers exist in a semi-crystalline form with crystallinity varying from 35 to > 70%, depending upon the preparation method. These crystalline forms of the polymer involve lamellar and spherulitic morphology [29]. Unique molecular configurations in comparison to other known synthetic polymers, they exhibit a complex crystalline polymorphism. Due to this polymorphism properties, they show five crystalline phases such as α, β, γ, δ and ε phases possessing different molecular conformations [30,31]. Out of the five phases mentioned above, α-phase is the most common nonpolar phase and the β- and γ-phases are the polar piezoelectric phases. The α-phase exists in *TGTḠ* (trans-gauche-trans-gauche) conformation and it is thermodynamically stable while the β-phase exists in TTTT (all trans) conformation and is thermodynamically metastable phase [28,32–34]. Amongst them, the electro active β/γ-phases are responsible for the different application of polymers such as sensors, actuators and electrochemical systems [35,36].

In this work, main aim is to prepare fuel cell membrane with low cost, high ionic conductivity with lower fuel crossover membrane through direct sulphonation of poly(vinylidene fluoride-co-hexafluoro propylene) P(VDF-co-HFP). Nonconducting polymer like HFP is functionalized with chlorosulphonic acid to prepare ionomer in the main chain for fuel cell applications. The evidence of sulphonation and its extent are understood from various spectroscopic techniques. Thermal and mechanical stability have been measured to obtain the suitability of the membrane. Electrical and water uptake have been measured to obtain the appropriateness of the membrane for fuel cell. Molecular level phenomena along with structural details have been revealed. Efficiency of the membrane has been worked out by making stacks of membrane electrode assembly and is found to be a good option for fuel cell application.

2. Experimental

2.1. Materials

Granules of poly(vinylidene fluoride-co-hexafluoro propylene) which is a commercially available copolymer of poly(vinylidene fluoride) were obtained from Ausimont, Italy and will be termed as HFP. 99% pure chlorosulphonic acid (HSO_3Cl, LOBA Chemical) was used for sulphonation on the backbone of the polymer. HPLC grade N,N′dimethyl formamide (Himedia) was used as a solvent for the preparation of membrane.

2.2. Preparation of membrane

The preparation of copolymer membrane was done through solution route; firstly a pre-determined amount of *HFP* granules were dissolved into a 30 ml of DMF solvent and was stirrer in a magnetic stirrer about 1 h at 60 °C. Thus, the obtained viscous slurry was poured on the Petri dish, the solvent was evaporated and resulting films were dried at 50 °C under vacuum for 20 h. Thus, the solid membrane of HFP (~80 μm thickness) was cut into small pieces using polymer cutter for Functionalization.

2.3. Functionalization of the membrane

HFP membrane was functionalized using 98% chlorosulphonic acid at different temperature and predetermined time. Finally, an optimized condition of functionalization was chosen so that mechanically stable polymer membrane was produced after the functionalization. The membranes change its colour to light brown to deep brown during the functionalization of the membrane followed by their immersion in deionized water, until the residual water pH becomes ~7 and adsorbed water on the membrane was shocked using tissue paper. Then, functionalized membrane was dried under the reduced pressure at 70 °C for 20 h. The sulphonation of membrane was done using two different temperatures of 65 and 75 °C for a fixed time period of 45 min. Henceforth; functionalized species will be termed as HFP-12, and HFP-18. The numbers after HFP indicate the degree of sulphonation, measured through NMR spectroscopy. Small pieces of membranes were mixed and make uniform thickness of ~80 μm of 4 × 4 cm^2 size using compression molding machine (S.D. Instruments, Kolkata, India) at 180 °C under 2.5 ton of pressure for fuel cell efficiency measurements.

2.4. Water uptakes

To measure the hydrophilicity of the membrane, percentage water uptake (WU) of the membrane was measured at 30 °C using 4 × 4 cm^2 size of the film. Firstly, weighed dry membrane was put on deionized water for 24 h at room temperature and water absorption was calculated from the following Eqn. (1);

$$WU\,(\%) = \frac{D_{weight} - D_{dry}}{D_{dry}} \times 100 \quad (1)$$

2.5. Ion exchange capacity (IEC)

To measure the ion exchange capacity (IEC) of functionalized membrane, firstly membrane samples were immersed in 2 M HCL solution to convert all sulfonated species into acidic form. The membranes were washed with double distilled water to remove the adsorbed acid. 2 M NaCl solutions were used for equilibrating the membrane for 24 h for ion exchange to take place. The remaining solution was titrated with 0.025 M NaOH solution using phenolphthalein as an indicator. The IEC values were calculated using the following equation (2) [15];

$$IEC = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}} \quad (2)$$

where, V_{NaOH} and C_{NaOH} are the volume and molar concentration of NaOH solution used for titration. W_{dry} is the weight of dried samples.