197. Inorganic-Organic Nano Composite Hybrid Membrane Based on Titania and Polystyrene for High Temperature PEM Fuel Cell

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Abstract

Low temperature PEM Fuel cells have limitations such as CO catalyst poisoning effect, Water and heat management, etc. These can be reduced by using high temperature PEM fuel cell (>90˚C). Therefore, it is need of hour that high temperature PEMFC must be focused. Inorganic-Organic Nano composite hybrid materials are among the top contenders to be utilized as membranes for high temperature PEMFCs. In this research, we have synthesized titania nanoparticles using TTIP precursor. For hybrid membrane, we have used polystyrene Mw 35000 and Poly (styrene-co-maleic anhydride), cumene terminated as polymers and Titanium dioxide Nano particles as inorganic filler. Wet chemistry route is used for Nano particle and hybrid membrane preparation. Synthesized membranes were characterized by using X-ray Diffraction and Scanning Electron Microscopy. The results showed that Titania based impregnated Polystyrene/PS-co-ma blend membranes exhibited good characteristics for its utilization as membrane for HTPEMFCs.

Keywords: *HT-PEMFC; Hybrid membrane; Polystyrene; Nano Particles;*

1. Introduction

Proton exchange membrane / polymer electrolyte membrane Fuel cell (PEMFC) is the promising fuel cell, which has application in portable devices, transport vehicles as well as in stationary power generations[1]. Power is generated in PEMFC through an electrochemical reaction in which oxygen reacts with hydrogen.

$$\text{At anode:} \quad 2H_2 \rightarrow 4H^+ + 4e^-$$

$$\text{At cathode:} \quad O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$

$$\text{Overall reaction:} \, 2H_2 + O_2 \rightarrow 2H_2O$$

The transfer of electron in this reaction is given an alternate path and which is collected as source of power while the H+ is passed through electrolyte membrane from anode to cathode. The membrane plays an important role, that it may let pass maximum of protons through itself while blocking the passage of electron.

Currently Nafion is used as PEMFC membrane which has high durability and operate well at temp below 90˚C, but it has some disadvantages like water and heat management, CO catalyst poisoning effect, high cost of membrane as well as Platinum Pt catalyst [2-4]

PEMFCs which can operate between 100˚C to 200˚C are known as HT-PEMFCs. HT-PEMFC can overcome above mentioned issues and it can also utilize the waste heat for cogeneration process[3].

Advantages of HT-PEMFC[2] includes fast reaction fast reaction kinetics, where Oxygen Reduction Reaction (ORR) is slow in LT-PEMFC which results in power losses due to the over potential at cathode, but in HT-PEMFC ORR reaction rate is high which results in improved efficiency.

Carbon monoxide CO tolerance issue is a serious issue in operation of LT-PEMFC. LT-PEMFC uses Platinum catalyst, which has strong affinity for CO, thus a little amount CO can cause degradation. The CO poisoning effect decreases with increase in temp, thus HT-PEMFC can overcome this effect. Heat management is another issue with LT-PEMFC operation, as half of energy produced is heat, which require its removal continuously because such heat above operating temp causes degradation of cell and require special costly management for its removal. HT-PEMFC can overcome these issues. the increased temperature can be controlled by existing Colling systems available in vehicles or in cogeneration as well as on-board reforming facility. Water management also remain a striking issue when operating at low temp, as both gaseous as well as liquid phase of water is present at low temperature. which cause it difficult to maintain the membrane humidification level maintained for efficient process. At high temperature operation only gaseous phase of water is present thus simplifying water management.

At high temperature the simpler heat and water management along with more CO tolerance and fast reaction kinetics made possible a simpler design of flow field and thus decreasing the overall cost of cell.

Currently Research is carried to develop electrolyte membrane for HT-PEMFCs which can operate above 100˚C near 120˚C as in accordance with US department of Energy guidelines for automotive applications[1]. Different polymers as well as organic-inorganic composite membranes had been developed and studied as alternate membrane for HT-PEMFC electrolyte applications[2,5].

Research work has also been carried on polystyrene and titania interaction like polystyrene encapsulation of TiO2 nanoparticles[6] and Titania impregnation into polystyrene resulted in better mechanical properties[7],also its interaction for photo catalyst environment resulted better[8]. In this research we have synthesized cost effective novel inorganic-organic composite membrane in which polystyrene and Poly (styrene-co-maleic anhydride), cumene terminated has been selected as polymers while titania TiO2 nano particles as inorganic fillers. For structural characterization XRD has been successfully performed, morphological study of membrane has also been performed using SEM.

2. Materials and Methods

2.1. Materials

The materials used in this experiment are Polystyrene Mw 35000 and Poly (styrene-co-maleic anhydride), cumene terminated Mn 19000 from Sigma Aldrich, THF (Tetra hydro Furan) from Fisher Scientific, TTIP Titanium (IV) Isopropoxide from Sigma Aldrich.

2.2. Methodology

Wet chemistry route has been used for TiO_2 nano particles as well as membranes. For synthesis of TiO_2 nano particles 5ml of TTIP was slowly added into solution of 75ml ETOH, 300ml deionized water and 1ml HCL. Kept the solution on slow stirring for 48 hours at room temperature. The precipitated TiO2 was filtered and dried and after grinding it the powder were calcinated at 400˚C for 3 hours in furnace.
For membrane preparation 1.5gram Polystyrene (PS) and 0.5gram PS-co-ma 10% solutions were prepared respectively in THF. After stirring for 3 hours, both solutions were mixed and kept further for 3hour at magnetic stirring. Prepared PS/PS-co-ma solution was then poured into glass petri dish and let the solvent to evaporate at room temperature. PS/PS-co-ma blend membrane was obtained by placing the petri dish in distilled water.
For PS/PS-co-ma/TiO2 membrane preparation, 10% solution of Titania nano particles in THF is kept for 1-hour sonication. Mix titania solution with PS/PS-co-ma solution prepared earlier and keep it for two hours at magnetic stirring. Prepared PS/PS-co-ma solution was then poured into glass petri dish and let the THF to evaporate. Smooth composite membrane was obtained after placing Petri dish in distilled water.

3. Results and Discussion

3.1. X-Ray diffraction (XRD) analysis

XRD studies were conducted to study the crystallinity of composite membrane. Fig.1(a). shows the pattern of TiO2 Nano particles Maximum Peak for pure Titania dioxide nano particles was observed at 2θ= 25.6˚ while others peaks were observed at 27˚, 37˚and 48˚. All peaks of titania nano particles were matched with PDF card # 75-1537. The broader peaks of titania is due to smaller crystallite size. Pure titania shows the tetragonal structure and anatase form. Fig.1(b) shows the pattern of composite hybrid membrane. The maximum peak for composite membrane was observed at 2θ =20˚and at 2θ=24.66˚. The composite hybrid membrane peak at angle 20˚ shows the polystyrene peak while that at 24.6˚ is of impregnated Titania nano particles. The composite membrane peaks were similar to the PDF card # 13-0843.

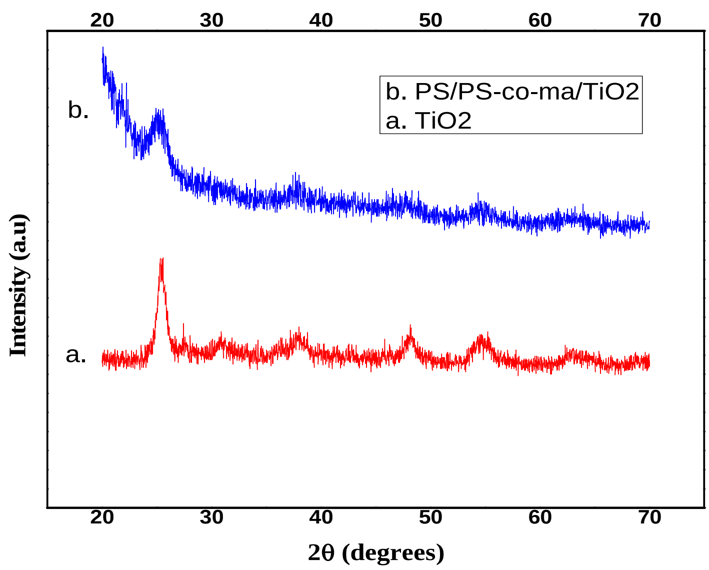

Fig. 1. XRD pattern of TiO_2 Nanoparticle and PS/PS-co-ma/TiO_2 composite membrane

3.2. Surface Morphology

Both pure and hybrid membrane were examined for morphological analysis via SEM. Morphology of Pure PS/PS-co-ma and titania doped PS/PS-co-ma has been shown in fig 2(a) and 2(b) respectively. Fine looking morphology was observed for pure PS/PS-co-ma membrane which shows smooth surface with almost no pores, thus non favourable for proton exchange purpose. On the other hand, morphology of composite membrane surface reveals that hybrid membrane has irregular morphology and Titania nano particles has been successfully impregnated. The morphology at high resolution shows very fine and dense distribution of nano sized pores in surface of composite membrane. The average pore size found to be 3-4µm. This distribution of fine pores provides a good pathway for conduction of protons throughout the electrolyte membrane between the electrodes.

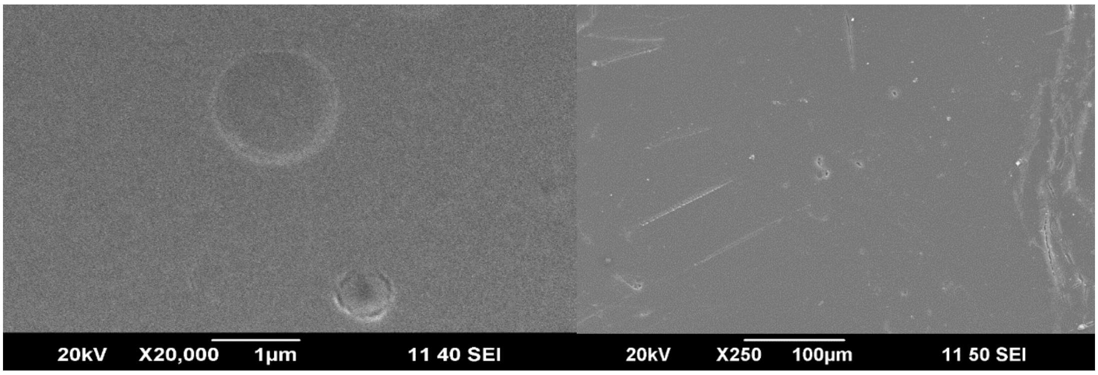

Fig. 2(a): SEM morphology of PS/PS-co-ma blend membrane

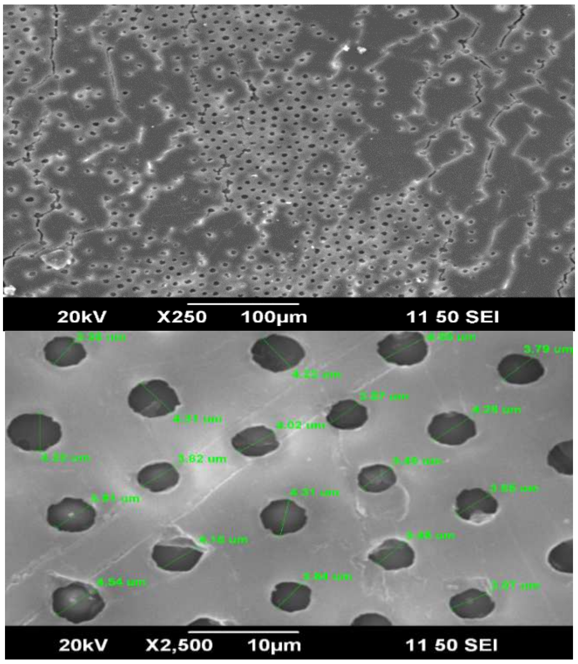

Fig. 2(b) SEM morphology of PS/PS-co-ma/TiO_2 composite hybrid membrane

Further characterization like proton conductivity measurement and thermal stability of this membrane can also be performed which may give us more insight of its behaviour.

4. Conclusion

TiO_2 nano particles and Organic-Inorganic composite hybrid electrolyte membrane for PEM fuel cell were successfully synthesized. From XRD analysis it was found that impregnation of inorganic Titania nano particles to the polystyrene blend has been done successfully. From SEM analysis it was concluded that The impregnation of titania has resulted in very fine and increased number of holes on surface of composite membrane for H+ transfer. The average hole size was found to between 3-4µm.

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