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Phosphonated SBA-15/Phosphonated PSEBS Composite Membranes for High Temperature Proton Exchange Membrane Fuel Cells

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ABSTRACT

Proton exchange membrane fuel cells (PEMFC) are increasingly becoming an attractive energy source for the future due to their portability, silent operation and high power density. Efforts have been made to improve their efficiency as well as in making the technology affordable. Several parameters come into play in the context of fuel cell efficiency, of which the operating temperature is of prime importance. Specifically, high temperature PEM fuel cell (HTPEMFC) has greater merits such as higher efficiency, improved tolerance of the electrodes against carbon monoxide poisoning, faster reaction kinetics, and effective heat transfer. Since the proton conductivities of commonly used perfluorinated membranes, such as Nafion, is highly dependent on external humidification, their operating temperature is limited to 100 °C. Hence one of the biggest challenges in PEMFC is fabricating a thermally stable membrane which can operate at temperatures above 100 °C under anhydrous conditions.

In the present work phoshonated SBA-15/phosphonated Poly(styrene-ethylene-butylene-styrene) (PSEBS) composite membranes are developed for high temperature fuel cell electrolyte. Mesoporous Santa Barbara Amorphous (SBA-15) was synthesized and it was grafted with phosphonate functionality using a simple two-step process involving chloromethylation and subsequent phosphonation. The phosphonated SBA-15 (PSBA-15) was characterized using Fourier transform infra-red (FTIR) spectroscopy, solid state 13C Nuclear magnetic resonance (NMR), 29Si NMR, 31P NMR for confirming successful modification. Morphology features were verified by small angle X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Transmission electron microscopy TEM analyses. Poly(styrene-ethylene-butylene-styrene) (PSEBS) was chosen as the base polymer and phosphonic acid functional groups were grafted onto the polymer using the aforementioned approach, where chloromethyl (-CH2Cl) groups were attached to the main chain using Friedel Craft's alkylation, followed by the phosphonation of the chloromethylated polymer by the Michaels-Arbuzov reaction resulting in phosphonated PSEBS (PPSEBS). The functionalisation was confirmed using NMR and FTIR spectroscopy studies. Composite PPSEBS/PSBA-15 membranes were fabricated with different filler concentrations (2, 4, 6, and 8%) of PSBA-15. Various studies such as water uptake, ion exchange capacity and the proton conductivity of the composite membranes were undertaken with respect to fuel cell applications. From the studies, it was found that the PPSEBS/PSBA-15 membrane with 6% wt of filler exhibited maximum proton conductivity of 8.62 mS/cm at 140 °C. Finally, membrane electrode assembly (MEA) was fabricated using PPSEBS/6% PSBA composite membrane, Platinium (Pt) anode, Pt cathode and was tested in an in-house built fuel cell setup. A maximum power density of 226 mW/cm2 and an open circuit voltage of 0.89 V was achieved at 140 °C under un-humidified condition.

Keywords: Phosphonated SBA-15, Functionalised SBA-15, Solid-state CP/MAS NMR, High-temperature polymer electrolyte fuel cell, Ion conducting membrane.

INTRODUCTION

Increase in the human population and rapid economic development in the last few decades have surged the energy demand around the world. This has resulted in rapid depletion of the fossil fuel resources and also have caused serious damage to the environment by the emission of greenhouse gases.

Hence, affordable and environment friendly sources of energy are highly critical at this juncture [1].With respect to clean energy harvesting, proton exchange membrane fuel cells (PEMFC) are increasingly becoming an attractive energy source for the future due to their portability, silent operation, and high power density [2]. Efforts have been made to improve their efficiency as well as in making the technology affordable. Several parameters come into play in the context of fuel cell efficiency, of which the operating temperature is of prime importance. Specifically, high-temperature PEM fuel cell (HTPEMFC) has greater merits such as higher efficiency, improved tolerance of the electrodes against carbon monoxide poisoning, faster reaction kinetics, and effective heat transfer [1, 3]. Since the proton conductivities of commonly used perfluorinated membranes, such as Nafion, is highly dependent on external humidification, their operating temperature is limited to 100 °C [4, 5]. Hence, one of the biggest challenges in PEMFC is fabricating a thermally stable membrane which can operate at temperatures above 100 °C or under anhydrous conditions.

Various methods have been reported regarding the development of high-temperature PEM such as usage of hydrophilic inorganic fillers like modified Silica, Titania, acid–base polymer blends, and functionalization of polymer side chains. Phosphoric acid (PA) doped polybenzimidazole (PBI) and poly 2,5-polybenzimidazole (ABPBI) have been reported by various researchers as acid-base polymer blends which shows conductivity values from ~ 10−12 S cm−1 to > 0.01 S cm−1 [6–10]. Leaching of PA and membrane stability is a critical issue and to overcome this problem, covalent grafting of phosphoric acid group has been reported. Several polymers such as polystyrene, polyphenylene oxide, polyimide, and polysulfone have been subjected to functionalization with phosphoric acid group and were used to fabricate hightemperature PEM [4, 11–14].

MATERIALS AND METHODS

PSEBS block copolymer (with Mn of 89,000 and Polydispersity index of less than 1.06), stannic chloride (SnCl4), triethyl phosphite (TEP), pluronic P123, (EO20PO70EO20), tetraethyl orthosilicate (TEOS), 3- chloropropyltrimethoxysilane, and diethyl carbitol (DEC) were obtained from Aldrich. Paraformaldehyde, chloroform, trimethychlorolsilane (TMSCL), stannic chloride, and methanol were obtained from E-Merck (India). 1,3,5-Trioxane was acquired from Alfa Aesar. Vulcan XC-72 (20% of Platinum in carbon support) was received from Arora-Mathey. Carbon cloth was obtained from Cobat carbon Inc. All the materials were used as received, without any further purification and double distilled water was used for all the experiments wherever required.

CONCLUSION

Mesoporous SBA-15 was synthesized and phosphonated through a simple two-step chloromethylation-phosphonation route. The successful synthesis and phosphonation of SBA-15 were confirmed by FTIR, NMR, BET, XRD, and SEM analyses. Composite membranes were synthesized by introducing PSBA-15 into the polymeric matrix phase composed of phosphonated PSEBS, wherein the latter was synthesized through the same reaction scheme. The thermal and mechanical properties of the membranes were studied, in addition to proton conductivity that were conducted to evaluate the potential offered by the composite membranes towards hightemperature PEMFCs. All the membranes exhibited good thermal and mechanical integrity, and high values of proton conductivity and the properties were found to improve proportionately with the filler concentration up to a certain extent. The PPSEBS/6% PSBA-15 showed an optimum combination of high proton conductivity, thermal and mechanical strengths. Typically, it showed a conductivity value of 8.62 mS/cm at 140 °C. MEA fabricated based on the composite membrane showed a maximum OCV of 0.86 V and amaximum power density of 226 mW/cm2 at 140 °C in a working fuel cell setup. High density of ion exchange groups in the composite membrane and the mesoporous morphology of the fillers helped facilitating proton conduction above 100 °C. These results show that the addition of phosphonated SBA-15 serves to overcome the limitations of polymer-based PEMs and offer a great potential towards high-temperature PEMFCs.

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