Colloids and Surfaces A 542 (2018) 8–14

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Nanoporous composite proton exchange membranes: High conductivity and thermal stability

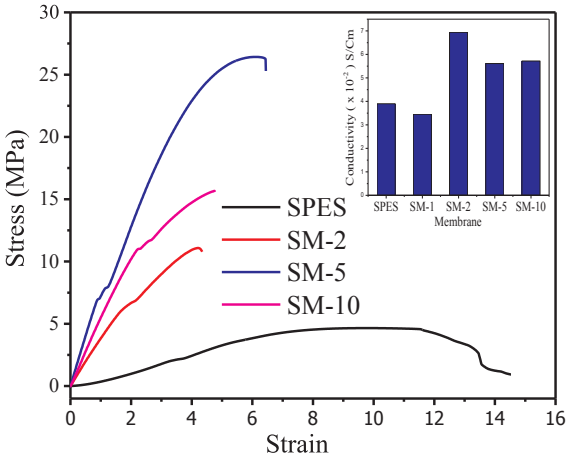
Swati Gahlot[a], Prem P. Sharma[a,b], Vikrant Yadav[a,b], Prafulla K Jha[c], Vaibhav Kulshrestha[a,b,*]

[a] CSIR- Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific and Industrial Research (CSIR), Gijubhai Badheka Marg, Bhavnagar 364002, Gujarat, India

[b] Academy of Scientific and Innovative Research, CSIR- Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific and Industrial Research (CSIR), Gijubhai Badheka Marg, Bhavnagar 364002, Gujarat, India

[c] Department of Physics, Faculty of Science, The MS University of Baroda, Vadodara 390002, Gujarat, India

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Polyethersulfone
MCM-41
Nanoporous PEMs
Proton conductivity
Thermo-mechanical properties

ABSTRACT

Nanoporous composite proton exchange membranes of sulfonated poly ether sulfone (SPES) and sulfonated mesoporous silica (S-MCM-41) have been prepared for energy based applications. Various weight % of Sulfonated MCM-41 has been incorporated in SPES matrix. The presence of surface functionalized MCM-41 as inorganic fillers in the SPES matrix, subsequently led to significant enhancement in the proton exchange capacity and proton conductivity of the nanoporous membranes. Nanoporous composite membranes have been subjected to various structural, thermal and mechanical techniques. Further developed membranes have been analyzed, for methanol permeability to evaluate membrane performance for fuel cell application. Methanol permeability of SM-2 is found to be $2.34 \times 10^{-8}\,cm^2\,s^{-1}$ which is very less than SPES revealing the suitability of composite membranes for fuel cell.

* Corresponding author at: CSIR- Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific and Industrial Research (CSIR), Gijubhai Badheka Marg, Bhavnagar 364002, Gujarat, India.

E-mail addresses: vaibhavphy@gmail.com, vaibhavk@csmcri.res.in (V. Kulshrestha).

https://doi.org/10.1016/j.colsurfa.2018.01.039
Received 23 November 2017; Received in revised form 18 January 2018; Accepted 18 January 2018

1. Introduction

An urge to develop and investigate new energy storage and energy generation devices is taking place due to continuously decreasing of renewable energy sources (coal, natural gases etc.). Fuel cells are a kind of energy generation devices that are being used in transportation and portable devices [1,2]. Proton exchange membrane (PEM) separating the electrolytes in a polymer electrolyte membrane fuel cell (PEMFC) is of enormous interest as it is responsible for better performance. Membrane prevent fuel of two compartments from mixing as well as permitting movement of protons. Key features that makes PEM efficient are low methanol permeability, high ionic conductivity, and chemical resistance with higher thermal and mechanical strength. Perflourinated nafion membrane is a knockout for fuel cell as an electrolyte. However, high cost, low methanol permeation resistance and degradation at high temperature of nafion limits their application for fuel cell systems [3]. Several other polymeric membranes have demonstrated potential for PEMFC [4,5]. Polymeric membranes display many drawbacks such as low chemical stability restricting their long term use etc.

In order to get PEMs with preferred performance, the nanoscale manupulation of ionic channels has been extensively studied [6]. Thus researchers came up with the idea of organic-inorganic composite membranes summing up the excellent features of both organic and inorganic materials [7,8]. It has been reported that many PEMs containing fillers have enhanced physicochemical and electrochemical properties compared to the membranes containing no filler [5]. Methanol crossover can be significantly reduced in direct methanol fuel cells (DMFCs) by nanocomposite PEMs [9,10]; and they can also effectively prevent the cross mixing of electrolytes in vanadium redox flow batteries (VRFBs) [11,12]. Regarding the synthesis of nanocomposite PEMs, different synthesizing methods have been developed, among which the physical blending method and sol-gel method are most commonly used [13]. Different theories have been proposed to explain the origin of property improvement for nanocomposite PEMs. Reports reveals that the functionalized nanomaterials can introduce extra ion exchange groups, which act as additional ion exchange sites. Both the ion exchange capacity (IEC) and ionic (proton) conductivity increase in nanocomposite PEMs. On the other hand reports suggests nanomaterials favors the formation of continuous ion channel networks inside the membrane matrices and the interconnection of channels inside PEMs [14].

A significant amount of work has been done to develop efficient nanocomposite polymeric membranes incorporating various materials such as graphene oxide (GO), carbon nanotube, MOFs etc. [15–17]. Ordered mesoporous silica MCM-41 is an excellent material possessing well defined mesoporous structure (2–25 nm), mechanical and thermal stability, high surface area etc. to consider as a material for preparing organic-inorganic composite [18,19]. As reported earlier MCM-41 has been used to improve selectivity and permeability of mixed matrix membranes [20,21]. Polymeric composite membranes have been fabricated so far by adding MCM-41 particles into the matrix for many applications. Further, sulfonic acid functionalization is considered to increase ionic conductivity. A report suggests that grafting sulfonic (SO_3H) groups to MCM-41 are favorable for high temperature fuel cell application [22]. Such additives have a high capacity storage of water useful for membrane based applications [23]. Wang et al. prepared MCM-41-ZIF-8/PDMS hybrid membranes for pervaporation application yielding a high flux 2204 gm/m^2 h and a separation factor of 10.4 for ethanol [24]. Mixed matrix membranes of SO_3 functionalized MCM-41 incorporated in sulfonated aromatic poly (ether ether ketone) (SPEEK) has been synthesized for CO_2 separation [25]. It has been shown that functionalized MCM-41 shows a good adherence with polymer matrix thus increasing both gas permeability and selectivity.

In this work we aim to design a new type of hybrid proton-exchange membranes by introducing inorganic fillers (S-MCM-41) to the SPES polymer matrix. The relationship among porosity/structure, physicochemical and electrochemical properties of the resultant membranes was investigated in detail. Membrane performance was then evaluated for methanol permeability for fuel cell application. Membranes were analyzed for structural, thermal, and mechanical properties.

2. Experimental

2.1. Materials and method

Poly (ether sulfone) Veradel® HC A-301 (PES) was purchased from Solvey Chemicals Pvt. Ltd., India. All other chemicals were obtained commercially and used as it is. Double distilled water was used throughout the study.

2.2. Synthesis and sulfonation of MCM-41 and membrane preparation

Synthesis of MCM-41 has been done through the process reported earlier [26]. Here, tetraethyl orthosilicate (TEOS) is added to the prepared aqueous solution of cetyltrimethylammonium bromide (CTAB) with constant stirring at room temperature and allowed to stir for 8 h. The obtained white gel is further heated for 24 h at 100 °C. This white solid was then filtered, washed and dried at 60 °C over night followed by calcination at 500 °C for 7 h. Sulfonation of MCM-41 has been performed through (3-Mercaptopropyl) trimethoxysilane (MPTS) as reported by Khan et al. and designated as S-MCM-41 [27]. Sulfonation of PES has been performed using H_2SO_4 as reported earlier [28]. Composite membranes of S-MCM-41 and SPES was synthesized by solution casting method. A definite amount of sulfonated silica was dispersed in N,N-Dimethylacetamide (DMAC) through sonication followed by dissolving SPES polymer by stirring for 2–3 h to prepare a homogenous solution followed by sonication (Scheme Scheme 11). This solution was then casted on glass plate and dried to synthesize membrane. After the membrane was dried it is peeled off from glass plate and stored. Quantity of S-MCM-41 (wt%) was varied in SPES matrix e.g. 1, 2, 5 and 10 wt% and designated as SM-n where n denotes the wt% of S-MCM-41 in SPES matrix.

2.3. Chemical and structural characterization

Membranes were characterized for various structural, thermal, mechanical techniques. Fourier-transform infrared (FTIR) of MCM-41, S-MCM-41 and prepared membranes was recorded with GX series 49387 spectrometer in a frequency range of 4000–400 cm^{-1} using KBr pellet method. X-Ray Diffraction (XRD) of prepared materials was done on Philips X'Pert MPD System using CuKα radiation with 0.15406 nm in scattering angle range of 1–20°. Scanning electron microscopy (SEM) was done for surface characterization of S-MCM-41 and the membrane cross section with Philips X'pert MPD System after gold sputter coating. Atomic force microscopy (AFM) images of developed membranes and MCM-41 was done using an NTEGRA AURA (NTMDT) instrument in semi contact mode with SPM NSG 01 tip with approx. 10 nm radius of curvature was used to estimate the surface roughness (natural frequency for the cantilever was 300 kHz).

2.4. Surface area and porosity of S-MCM-41

Surface area and porosity of the sample was measured by a volumetric gas sorption system (Micromeritics Instrument Corporation, USA, model 3Flex). N_2 adsorption/desorption isotherms were recorded at analysis bath of liquid nitrogen temperature (77 K) upto 1 bar. Prior to the measurements, the sample was activated (degassed) by heating at the rate of 1 K/min upto 393 K under vacuum. The temperature as well as vacuum was maintained about 6 h prior to the measurement. As silica platform was functionalized with organic moiety, the temperature of 393 K was chosen so as to protect organic moiety from destruction.