Colloids and Surfaces A 538 (2018) 622–627

Contents lists available at ScienceDirect

Colloids and Surfaces A

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

Research paper

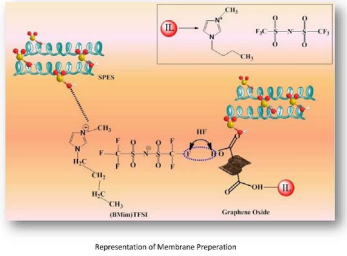
Ionic liquid grafted graphene oxide composite to create proton transfer pathways in polymer electrolyte membrane

Swati Gahlot[a], Prem P. Sharma[a,b], 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

GRAPHICAL ABSTRACT



Representation of Membrane Preperation

ARTICLE INFO

Keywords:
Ionic liquid
SPES
PEMs
Durability
Proton conductivity
Fuel cell

ABSTRACT

For the synthesis of polymer electrolyte membrane (PEM), high ionic conductivity and stability are the key challenge. This paper deals with the preparation of polymer electrolyte membranes based on ionic liquid (IL) functionalized graphene oxide (GO) and sulfonated polyether sulfone (SPES). Using a simple solution casting technique, composite membranes have been prepared possessing good physicochemical properties and mechanical stability. Methanol crossover resistance have been measured across the composite membranes and found to be low for IG- 05 membrane (0.53×10^{-7} $cm^2\,s^{-1}$) with the selectivity of 7.99×10^5. Composite IG-05 membrane also exhibit high ionic conductivity of 7.27×10^{-2} $S.cm^{-1}$ which is around 66% higher than that of SPES membrane.

1. Introduction

Depletion of non renewable sources of energy have generated the requirement to exploit alternative power sources such as fuel cell. Polymer electrolyte membrane fuel cell (PEMEC) are under progression for energy generation application like portable or stationary power system, transportation etc. due to the limited conventional energy sources [1,2]. Fuel cells convert the chemical energy into the electrical energy, consists of a polymer electrolye membrane (PEM) as a critical component [3–5]. Nafion is commercially available PEM, due to limitation of nafion at higher temperature and its high cost, attracts the researcher to synthesize new PEM with low cost and high stability.

The fascinating discovery of graphene, a two dimensional material, has opened up new doors of possibilities for science and technology. Exhibiting unique thermal, mechanical, optical properties graphene has become a material of interest to explore new possibilities in various applications. Single layered structure and pure carbon composition make graphene an inimitable material [6]. Graphene oxide, easily

* 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: vaihavphy@gmail.com, vaibhavk@csmcri.res.in (V. Kulshrestha).

https://doi.org/10.1016/j.colsurfa.2017.11.060
Received 26 September 2017; Received in revised form 17 November 2017; Accepted 20 November 2017
Available online 21 November 2017

synthesized by Hummer's method, has found potential applications in diverse fields such as energy conversion and storage, separation, bio sensors etc [7–10]. As energy is one of the most concerned topic of today's era, considering the dwindling non renewable sources of energy. There is always a need to develop a PEM containing excellent features suitable for PEMFC including chemical and thermo-mechanical stability.

Nanocomposite materials are considered to possess excellent properties. Functionalization is one of the effective way to augment the overall property of the composite material. Graphene oxide (GO) has been functionalized with various materials such as metal oxide, inorganic materials etc. to improve its performance [11,12].Ionic liquids (IL) are salts in liquid form comprising many potential applications [13,14].Nanocomposite based on graphene and ionic liquid may lead to the formation of material with superior properties [15]. Incorporating fillers in polymer matrix improve the thermal and mechanical stabilities of the polymer [16,17]. Various IL based membranes have been developed that illustrate high ionic conductivity and can be operated at high temperatures [18,19]. Ye et al. have prepared composite polymer electrolyte membranes of graphene modified with protic ionic liquid, membranes shows dramatic enhancement in mechanical properties and ionic conductivities [20]. In another study by Mo et al. GO surface has been modified with IL by self-assembly and reduced further to enhance its mechanical properties [21]. Nanocomposite membranes of funcationalized graphene oxide and sulfonated poly(ether ether ketone) (SPEEK) polymer has also been prepared followed by impregnation with ionic liquid [22]. Mondal et. al reported the enhancement in proton conductivity in protic ionic-liquid (IL) based PEMs under anhydrous state and found the conductivity 0.57 mS cm^{-1} at room temperature, which increased considerably to 18.94 mS cm^{-1} at 150 °C [23]. In this manuscript, crosslinked graphene oxide/ionic liquid composite based polymer electrolyte membrane has been synthesized using sulfonated polyether sulfone (SPES) as polymer matrix for higher conductivity and stability.

2. Experimental

Ionic liquid, 1-Butyl 3-methylimidazolium bis(trifluoromethylsulfonyl) imide (BMIM TFSI), graphite powder and AIBN (2.2′-Azobis(2-methyl-propionitrile)) are purchased from Sigma Aldrich. Poly (ether sulfone) (PES) is obtained from Solvay Chemicals Pvt. Ltd., India. All other chemicals are obtained commercially. Deionized (DI) water is used throughout the experiment.

Graphene oxide (GO) was prepared by Hummer's method as described in our previous manuscript [7]. IL is grafted on GO according to the following procedure: 100 mg GO is dispersed in 12.5 ml methanol by sonicating for 4–5 h. Further, 105 mg of IL and 3.45 mg AIBN were added to above solution and refluxed at 80 °C under nitrogen for 16 h. Product was then filtered, washed with DI water followed by washing with acetone. Obtained product was dried, stored and designated as IL-GO. Sulfonation of PES was done to obtain sulfonated poly ether sulfone (SPES) as described earlier [24]. Composite membranes were prepared by dissolving a definite quantity of IL-GO in N,N'-dimethylacetamide (DMAC) and SPES polymer followed by ultrasonication. Nanocomposite membranes were prepared containing different quantity of IL-GO in SPES matrix i.e. 0.1, 0.2 and 0.5 wt% and named as IG-01, IG-02 and IG-05 respectively. Pristine membrane of SPES was also synthesized and named as SPES.

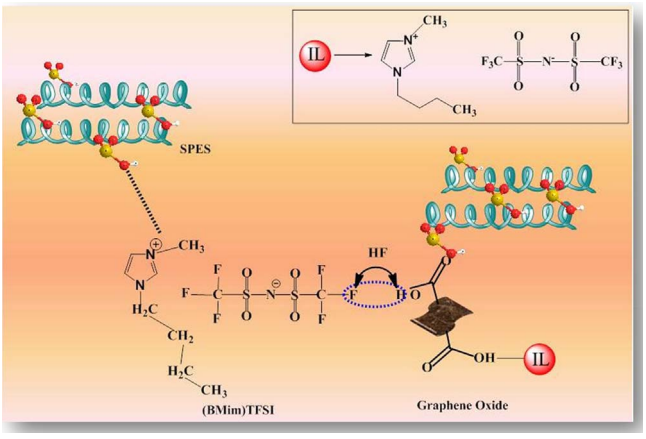
Chemical and structural characterization of GO, IL-GO and composite membranes have been performed by the means of FTIR, SEM, TEM and XRD analysis. Thermal and mechanical stabilities were carried out through TGA, DSC, DMA and UTM analysis and the details are included in electronic supplementary information (ESI) section. Water uptake was determined by measuring the weight gain after equilibrating in water for 24 h. Proton exchange capacity (PEC) was estimated by acid base titration. Proton conductivity of the membranes was determined by the membrane resistance measurements. Methanol permeability was evaluated in recirculation mode in two compartment cell. The details are included in electronic supplementary information (ESI) section.

3. Result and discussion

IL grafted GO has been prepared by dispersing GO powder in methanol and sonicating for homogenous solution followed by addition of IL and AIBN, refluxing under nitrogen. Scheme 1 depicts the interaction between IL (BMIM TFSI), GO and SPES. In this approach, anionic part of IL interact with GO.

For synthesis of composite membranes, IL-GO has been dissolved in DMAC by ultrasonication and SPES polymer is added further to prepare membranes by solution casting. Black-brown colored membranes are obtained after drying. Since SPES possesses $-SO_3H$ functional group in polymer backbone, cationic part of IL may interact with these free sites through hydrogen bonding. Both the cationic and anionic sites of IL are bounded through SPES and GO respectively thus leaving less possibility for leaching out. Before performing the experiments, membranes are treated with water at 70 °C to remove the uncrosslinked IL from the membranes. Within IL grafted GO composite membranes, IL may exist in two states: free- state and bound state. The former is related to the ILs having weak or no interaction with polymer matrix, which possess free mobility; the latter is related to the IL having strong interaction with the polymer matrix, restricting the leach out. Accordingly, it is ventured that the fast IL release might be mainly attributed to the release of free-state ILs.

FTIR spectroscopy provides information about the functional groups absorbed by the material. Fig. 1 evidences the FTIR spectra of GO and IL-GO. Peaks originated at 3428, 1726 and 1574 cm^{-1} in GO corresponds to O—H, C═O and C═C vibrational bands [25]. In GO peaks at 1192, 1023 cm^{-1} represents C—O epoxy, C—OH stretching mode of sp^2 skeletal network. After modification with ionic liquid, some new peaks appear in IL-GO suggesting the functionalization of IL on GO sheets. Due to the addition of IL to GO, there is a peak shift which may be attributed to π-π stacking. For IL-GO, band at 2927 cm^{-1} corresponds to C—H stretching, vibration at 1625 cm^{-1} is due to imiazolium framework. Vibration at 1384 and 1244 cm^{-1} are assigned to SO_2 [26].Peaks at 874 and 599 cm^{-1} are due to vibration of C—H of cyclic BMI+ [27]. Fig. 2 displays the FTIR spectra of prepared IL-GO composite membranes. On addition of IL-GO to SPES some new peaks emerges in FTIR spectra of composite membranes. Peak shift is also observed in IG-01 and IG-05 attributable to the interaction between IL-GO and SPES matrix. Broad peak near 3400 cm^{-1} in SPES is due to O—H stretching which is observed at 3430 and 3436 cm^{-1} in IG-01 and IG-05 respectively. This shift is because of the addition of IL-GO.



Scheme 1. Schematic representation of membrane preparation.