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Anion exchange composite membrane based on octa quaternary ammonium Polyhedral Oligomeric Silsesquioxane for alkaline fuel cells

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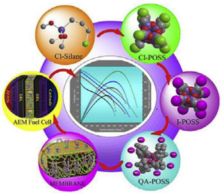
HIGHLIGHTS

- Octa quaternary ammonium POSS(QA-POSS) was synthesized and well characterized.
- QA-POSS filler loading in QPSU was optimized.
- Composite membranes showed high IEC, conductivity with minimal water uptake.
- Presence of QA-POSS nanoparticles in QPSU matrix showed improved performance.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of novel composite anion exchange membranes were prepared via simple solution casting method using synthesized quaternary ammonium functionalized Polyhedral Oligomeric Silsesquioxane (QA-POSS) with Quaternary polysulfone (QPSU). QA-POSS was synthesized from prepared Cl-POSS and well characterized by FT-IR, NMR, SEM and TEM analyses to confirm the chemical modifications and cubic morphologies. The QA-POSS nano particles have dual role in the membrane providing additional ion conducting groups and reinforcing the membrane in molecular level for the overall improvement of composite membrane. Additionally, the composite membranes were characterized by XRD, SEM, Ion exchange capacity (IEC), water uptake and conductivity to ensure the suitability of its use as an electrolyte in alkaline fuel cell. Finally, membrane electrode assembly (MEA) was fabricated using Pt anode ($0.25\ mg/cm^2$), Ag cathode ($0.375\ mg/cm^2$) and various synthesized composite membranes, and then it was tested in real time fuel cell setup. The membrane with 15% QA-POSS showed the maximum power density of 321 mW/cm^2. The results showed that QA-POSS possess the ability to enhance the performance of the anion exchange membrane significantly.

1. Introduction

As a result of the rising anxiety on the exhaustion of fossil energy sources and environmental issues, renewable energy technology is garnering a great extent of attention in last two decades [1,2]. Among various technologies, fuel cells have occupied a prominent place due to their high efficiencies, low emissions and revolutionary change in the field of electricity [3,4]. Proton exchange membrane fuel cells (PEMFCs) have been established in some portables, transportation and stationary power applications [5]. Regrettably, their high expensive material cost (need of noble metal catalyst) has hindered their widespread commercialization.

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Furthermore, their high fuel permeability behavior and poor electrode reaction kinetics leads to lower efficiency [6,7]. In contrast, anion exchange membrane fuel cells (AEMFCs) are believed as a possible alternative to overcome the barriers of PEMFCs in terms of cost, catalyst stability and efficiency that could potentially lead to the next generation of fuel cell technologies [8]. Anion exchange membrane (AEM) is the fundamental component of the AEMFC in which, the cation groups are covalently bonded to the polymers and surrounded by mobile, negatively charged hydroxide (OH^-) groups. Even though AEMFCs offer some prospective advantages, their lower ionic conductivity and lack of structural integrity (chemical stability) compared to PEMFCs is a matter of concern because it may perhaps lower the efficiency and durability of the fuel cell [9].

To conquer such challenges, many efforts have been dedicated to the development of AEMs possessing good hydroxide conductivity with reasonable mechanical properties [10]. Till now two approaches have been employed in the development of AEM via, 1) synthesis of novel polymer electrolytes containing different polymer backbones and cationic head groups [5,11,12]. 2) Synthesis of hybrid membranes by incorporating suitable fillers into the existing membrane to improve water uptake, ion exchange capacity and stability of the membrane at elevated operating conditions [13–15]. In the former approach, all but a few cationic head groups have been studied including ammonium [16], phosphonium [17], sulphonium [17], pyridinium [18], imidazolium [19], guanidium [20] with different polymers. However, no clear strategy exists in obtaining a durable AEM that maintains high ionic conductivity under dynamic conditions, for instance, temperature and humidity. Developing the hybrid membranes is a simple and effective technique for the development of high-performance AEMs. Fillers such as SiO_2 [21], TiO_2 [22], ZrO_2 [23], graphene [24], bentotite [25] and montmorillonite [26] have been incorporated into the AEM to improve the physico-chemical properties. Fillers play two roles in the membranes: First they increase the hydrophilicity of the membrane by absorbing water molecules resulting in an increased conductivity through hopping mechanism. Second, they reinforce the polymer matrix by forming chemical or physical bonds that improve the mechanical and thermal stability of the membranes [27].

AEMs with high ion conductivity could only be achieved in materials with high ion exchange capacity (IEC) and high water uptake [28]. Recent studies show that the fillers functionalized with cationic head groups have a greater tendency to increase the conductivity significantly, by involving in the ion exchange process [29–31]. In particular, porous materials are highly appreciable due to their porous nature (holds high amount of water) and high surface area (a large number of ion exchange groups can be attached) [32]. Such membranes also suffer from swelling and hence maintaining their mechanical properties in hydrated state for a long time becomes difficult. Thus, enhancement of conductivity with limited water uptake to attain higher efficiencies remains a daunting confront in the field of AEM [28].

The objective of this work is to prepare high ion exchange capacity membranes with controlled water swelling to achieve both fast ion transport and membrane stability concurrently. This can be achieved by incorporating quaternary ammonium functionalized Polyhedral Oligomeric Silsesquioxane (POSS) in the existing quaternary ammonium Polysulfone (QPSU) based anion exchange membrane. POSS is a new class of hybrid nano material, containing three-dimensional cage structure (diameter 1.5–3 nm), made-up of Si-O atoms as core with organic substitution [33]. POSS was selected due to their nanoscopic size, easy solubility in organic solvents (excellent capability to reinforce membrane) and the organic substitutions can be tuned to ion conduction groups [34]. We postulated that a hydrophilic ammonium group facilitates a favorable ion channel for efficient hydroxyl conduction while POSS basic core (Si-O-Si cage) with a strong hydrophobic domain would impair the high water swelling, leading to the maintaining of its mechanical strength. The present work describes the synthesis of a unique type of POSS with ion conductive capacity and its effect on the anion exchange membrane at different weight loadings has been evaluated.

2. Materials and methods

Preparation of QPSU was described in our previous study [35]. 3-Chloropropyl trimethoxysilane and di-*n*-butyltin dilaurate were obtained from Sigma-Aldrich. Sodium iodide, solvents like dimethylformamide, chloroform, methanol and triethylamine were purchased from E-Merck (India). Vulcan XC-72 (20% of Platinum in carbon support) was purchased from Arora-Mathey. Carbon cloth was obtained from Cobat carbon Inc.

2.1. *Experiments*

2.1.1. *Synthesis of octakis (3-chloropropyl) silsesquioxane (Cl-POSS)*

Cl-POSS was synthesized as per earlier procedure described elsewhere [36] and the same is described briefly below. In a two-necked round-bottom flask equipped with an additional funnel, a mixture of 300 ml of dry methanol and 10 mL of concentrated HCl was added and stirred for 30 min at 0 °C. To this, 3-chloropropyl trimethoxysilane (30 g, 0.15 mol) was added drop wise through an additional funnel over a period of 30 min and stirred for 2 h. The reaction mixture was kept at room temperature without stirring for the complete hydrolysis of the methoxy group. After 48 h, di-n-butyltin dilaurate (0.3 g, 0.48 mmol) catalyst was added for the self-condensation of the silanes. The reaction mixture was stirred for another 48 h at room temperature. A white precipitate was formed which was separated by filtration and then washed with methanol thrice to remove the impurities. It was finally dried in vacuum to obtain Cl-POSS.

2.1.2. *Synthesis of octakis (3-iodopropyl) silsesquioxane (I-POSS)*

Cl-POSS (5 g) and sodium iodide (10 g) were dissolved in dry THF (100 ml). The reaction mixture was stirred in the dark at 60 °C for 72 h, such that the Cl atoms are completely displaced by the I atoms [37]. After evaporating THF, the crude product was extracted with $CHCl_3$ and H_2O. The $CHCl_3$ layer was passed through sodium sulphate to remove the water content and then through sodium thiosulphate to remove the unreacted iodide. After evaporation, a dirty white solid of I-POSS was obtained.

2.1.3. *Synthesis of octakis triethyl propyl ammonium POSS (QA-POSS)*

4 g of I-POSS was dissolved in a two-necked round bottom flask containing 50 ml of DMF under inert (N_2) atmosphere. To this, 20 ml of triethylamine was added drop wise using an addition funnel and the reaction mixture was heated to 60 °C. After 24 h, the reaction mixture was subjected to vacuum drying to evaporate the solvent and the excess of trimethylamine to get a brown yellow sticky solid (QA-POSS) (see Fig. 1).

2.2. *Synthesis of composite membranes*

Composite membranes containing different weight percentages of QA-POSS (5, 10, 15 and 20%) were prepared as follows. The quaternary ammonium functionalized polysulfone (QPSU) ionomer in Cl^- exchangeable form was dissolved in DMF and the required amounts of QA-POSS were added and stirred for 48 h for the