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Stable and hydroxide ion conductive membranes for fuel cell applications: Chloromethyaltion and amination of poly(ether ether ketone)

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ABSTRACT

Poly(ether ether ketone) (PEEK) was dissolved in conc. H_2SO_4 and its chloromethylation was achieved in presence of paraformaldehyde, trimethylchlorosilane and Lewis acid catalyst, obtained about 35–75% degree of chloromethylation (DCM). This idea is based on partial sulfonation of PEEK to make it soluble and further complete replacement of $–SO_3H$ with $–CH_2Cl$ groups. Alkaline membranes (AMs) were prepared by quaternization of chloromethylated PEEK (CMPEEK). The reported method is a "green" alternative for the production of AEM without the use of hazardous chemicals (such as chloromethyl methyl ether, chloromethyloctylether, *bis*(chloromethyl) ether etc.). Chronopotentiometry study of prepared membranes confirmed their homogeneous and alkaline nature suitable for methanol fuel cells. The AMs exhibit a splendid chemical stability at 10 M KOH. Alkaline conductivity of quaternized poly(ether ether ketone) membrane with 75% DCM (QPEEK-75) (14.63 mS cm^{-1}) in equilibration with deionized water was relatively high in compare with other AMs reported in the literature. For the H_2/air single fuel cell at 50 °C with QPEEK-75 membrane, about 1.02 V OCV and 48.09 mW cm^{-2} power density at 109.3 mA cm^{-2} current density were obtained.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising energy conversion devices due to their high energy-conversion efficiency, power density, and low pollutant emission [1–3]. However, high cost, fuel loss and low durability of the electro catalysts in PEMFCs hampered their commercialisation [4,5]. Recently, significant attention has been rendered for alkaline membrane fuel cells (AMFCs), because of their potential to solve fundamental problems of PEMFCs [6–9]. In AMFCs, alkaline membranes (AMs) serve as hydroxide (OH^-) conductor and separator for fuel and oxidant. Several types of polymers, such as poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), copolymer of chloromethylstyrene and divinylbenzene, PVDF-vinylbenzyl chloride, and poly(vinyl alcohol)–poly(1,3-diethyl-1–1-vinyl imidazolium bromide), grafted poly(hexafluoropropylene-*co*-tetrafluoroethylene) (FEP) [10,11], and copolymer of poly(acrylonitrile), were used for the preparation of AMs [12–21]. For developing AMs, chloromethyl groups were introduced via electrophilic-substitution reaction, followed by quaternization. Chloromethylation was achieved by chloromethyl ethers or dihalomethyl ethers. Thermally and chemically stable high performance polymers (polysulfone or PEEK) based AMs were also prepared by chloromethylation with chloromethyl ether or chloromethyl–octylether, respectively [22,23]. In these methods, preparation of AMs was achieved by chloromethylation using chloromethyl ether (CME) followed by amination with a tertiary amine. In chloromethylation, the CME used is carcinogenic and potentially harmful to human health [14,24]. Also, chloromethylation of poly(sulfone) has been reported by mixture of paraformaldehyde, trimethylchlorosilane and a Lewis acid ($SnCl_4$) [25]. But, no attention was rendered to achieve the chloromethylation of PEEK using non-hazardous chemicals.

PEEK is insoluble in organic solvents, thus its partial sulphonation seems to be suitable option to achieve the high degree of chloromethylation. But, extra care should be necessary to control the degree of sulfonation and further complete replacement of $–SO_3H$ with $–CH_2Cl$ groups to avoid zwitterionic properties. By varying the reaction time, temperature, acid concentration and PEEK content, degree of sulfonation can be easily controlled [26–30]. Reported method avoids the use of hazardous and carcinogenic chemicals. Proposed reaction is diversified in nature and can be used for developing anion-exchange membranes or functionalized polymers.

2. Experimental section

2.1. Materials

Polyether ether ketone (PEEK, medium melt viscosity grade 450PF; Victrex PLC (England), stannic chloride, paraformaldehyde,

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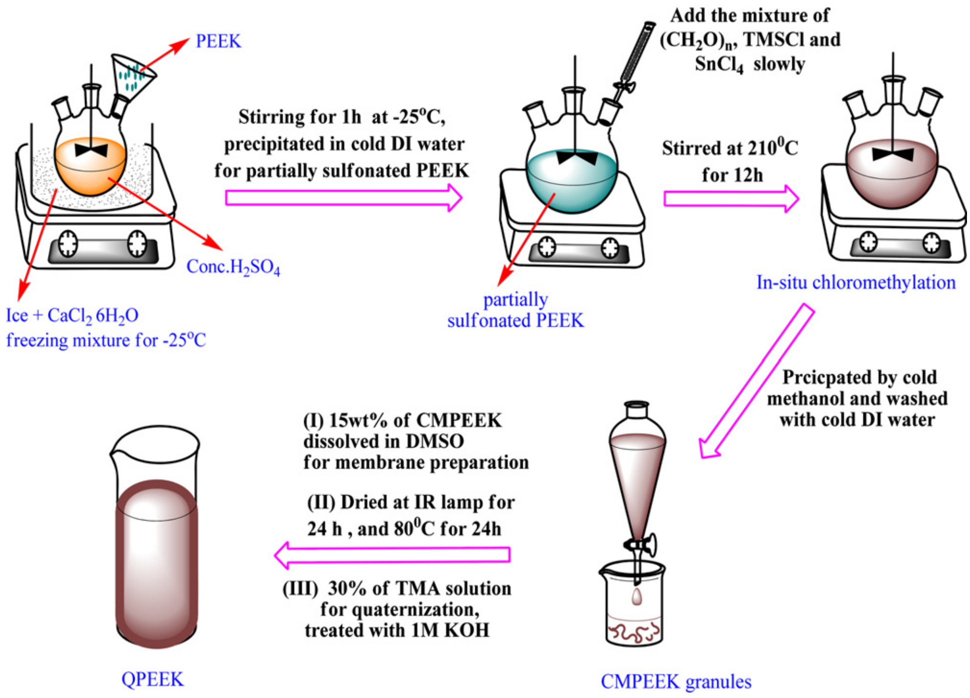

Fig. 1. Schematic presentation for CMPEEK and QPEEK synthesis.

trimethylsilylchloride (TMSCl), methanol, ethanol, sulphuric acid (98%), *N*,*N*-dimethylformamide (DMF), dimethyl acetamide (DMAc), dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), and trimethylamine (TMA) (AR grade; SD Fine Chemicals, India) were used as received. Distilled deionized water was used for all experiments.

2.1.1. *Synthesis of CMPEEK*

Synthesis procedure for CMPEEK has been depicted in Fig. 1. PEEK was dissolved in conc. H_2SO_4 (20 wt%) in a cooling bath at $-25\ ^{\circ}C$ temperature for 1 h. Reaction was achieved at extremely low temperature for controlling the degree of sulfonation in precise manner. The reaction mixture was precipitated in cooled water, to obtain partially sulfonated PEEK. The partially sulfonated PEEK was dissolved in a NMP (10 wt%), in-situ chloromethylation was carried out by using paraformaldehyde, TMSCl and $SnCl_4$ at 210 °C under stirred condition for 12 h. Reaction mixture was precipitated in chilled methanol to obtain final product (CMPEEK), followed by washing in cold water to remove impurities.

2.1.2. *Preparation of AMs*

Synthesized CMPEEK was dissolved in DMSO (15 wt%) to cast thin film of desired thickness onto a cleaned glass plate (Fig. 2). Obtained thin film was dried under IR lamp for 24 h and aminated with TMA solution (30%) for 24 h. These alkaline membranes were further treated with 1 M KOH solution for 24 h. Conditioned membrane was subjected for physicochemical and electrochemical characterization. Prepared AMs were designated as QPEEK-*X*, where *X* is the degree of chloromethylation (%).

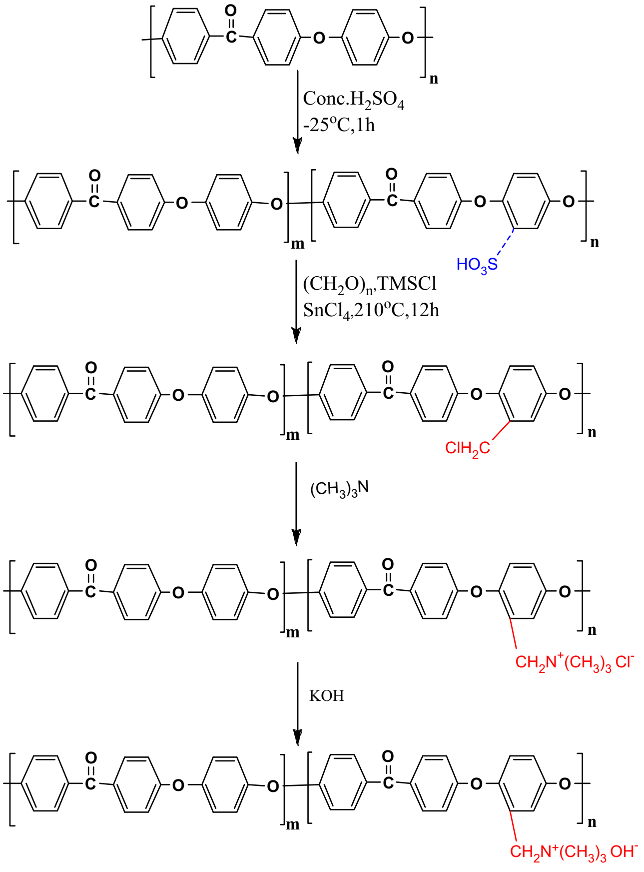

Fig. 2. Schematic presentation for the synthesis of QPEEK-OH.

2.2. *Instrumental characterizations*

The ^{1}H NMR, ^{13}C CP/MAS (cross polarization/magic angle spinning) spectrum of chloromethylated PEEK was recorded by NMR spectrometer (Bruker, 200 MHz for ^{1}H NMR and 125 MHz for CP/MAS), Fourier transform infrared (FTIR) spectra were recorded with spectrum GX series 49387 by ATR techniques. The elemental analysis (CHNS) was carried out using Perkin-Elmer-2400 CHNS analyzer for the percentage composition of the elements. Scanning electron microscopy (SEM) images of the