

Preparation of Sulfonated Monomer for Pem Fuel Cell and Solvent Optimization for Recrystallization

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Abstract: Polymer exchange membrane fuel cells are promising new power sources for vehicles and portable devices. Membranes currently used in PEMFC are perfluorinated polymers such as Nafion®. Even though such membranes have demonstrated good performances and long-term stability, their high cost and methanol crossover makes them unpractical for large-scale production. Sulfonated aromatic polymers based membranes have been studied due to their good mechanical properties, thermal stability and conductivity. In this study, sodium 5, 5'-carbonylbis (2-fluorobenzene- sulfonate) was performed as a sulfonated monomer contained sulfonic group which is considered as the base for proton exchange process of membrane fuel cell. Sulfonation of 4,4-difluorobenzophenone with 20 % fuming sulfuric acid by adding the SO₃ grouping to an organic molecule in such a way that sulfur is linked to the carbon through an oxygen bridge by the aromatic nucleophilic substitution reaction. Recrystallization of the produced sulfonated monomer was then studied using different types of solvents as methanol, ethanol and isopropanol, as well as, studying the ratio of (water: alcohol) mixtures as solvents. By studying the yield of the produced sulfonated monomer, it was found that 88% yield was obtained using 1:6 (water: ethanol) solvent mixture as an optimum solvent for the re-crystallization process.

Key words: Proton exchange • Fuel cell membrane • Sulfonation • Electrophilic aromatic substitution • Recrystallization

INTRODUCTION

Proton exchange membrane fuel cells (PEMFC) are promising power sources for both stationary and dynamic applications. Proton exchange membrane (PEM) regarded as the key component of fuel cell system. It is very important, because its stability which can withstand the harshing chemical and physical environment. The principle of fuel cells is based on the reverse reaction of electrode composition of water. In other words, electric power is generated when hydrogen and oxygen react on the cathode of the fuel cell. In order to carry out the reaction in an efficient way, hydrogen is ionized to a proton using a platinum catalyst on the anode and the proton or hydronium ion (HO⁺) dissociates at the anode and migrates through a proton-conducting electrolyte to the cathode [1, 2]. Several studies have been reported on sulfonated polymers used as a PEM material in both hydrogen and direct methanol fuel cells. In addition, blend polymer membranes and organic-inorganic membranes as the major component have been explored with the goal to

obtain good mechanical properties, high proton conductivity and optimized membrane properties. However, these materials usually prepared with post sulfonating polymers, which not only degrade the mechanical and thermal stability, but also lack the controlling of sulfonated process. So the direct sulfonation method has proven to be more advantageous than post-sulfonation due to its ease of control over the degree of sulfonation in the copolymerization step [2-4]. Also this method avoids cross-linking and other side reactions.

Sulfonated poly ether ether ketone (SPEEK) membranes are prepared by the method of direct synthesis of sulfonated monomer for fuel cell applications. The proton conductivity of SPEEK-based materials depends primarily on the degree of sulfonation (DS), which represents the content of -SO₃H per all possible -SO₃H substitution sites [5, 6]. The DS (no. of sulfonic group per repeating unit) can be determined by nuclear magnetic resonance ¹H (NMR) spectroscopy. Sulfonated polymeric membranes were

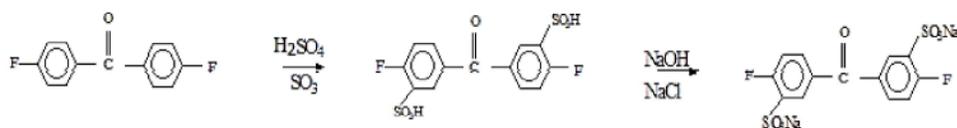
prepared by direct synthesis of sulfonated monomer and evaluated for fuel cell applications. This paper describes the preparation of sodium 5, 5'-carbonylbis (2-fluorobenzene-sulfonate) by sulfonation process of 4, 4'-difluorobenzophenone. As it is often difficult to decide upon the best solvent; the solvent is often chosen by experimentation, then the effect of solvent and (solvent: water) ratio used were studied in the re-crystallization process on the percent yield of obtained sulfonated monomer wherein water is still necessary to ensure removal of inorganic impurities in the product which are not appreciably soluble in the used solvents.

MATERIALS AND MEASUREMENTS

4, 4'-Difluorobenzophenone was purchased from Aldrich Chemical Co. and used as received. Fuming sulfuric acid (20% SO₃) purchased from Kanto Chemical Co. Other reagents and solvents were obtained commercially and used without further purification. Samples for Fourier transform infrared spectroscopy analysis (FT/IR-6100 type Jasco Japan TGS detector with the absorbance technique ranging from 400 to 4000 cm⁻¹ with scanning speed of 2mm/sec.) were prepared by blending 198 mg of IR spectroscopic grade KBr and 2mg of produced sulfonated salt.

Synthesis of Sodium 5, 5'-Carbonylbis (2-Fluorobenzene-Sulfonate): The synthesis of sodium 5, 5'-carbonylbis (2-fluorobenzene-sulfonate) was performed according to a procedure described by Miyatake *et al.* [6], Hasani-Sadrabadi *et al.* [7] and Wang *et al.* [8]. As shown in Scheme 1 and process flowchart (Fig. 1), 21.8 g (0.1 mol) of 4, 4'-difluorobenzophenone was dissolved in 20% fuming sulfuric acid (100 ml). The solution was stirred at 110°C for 6 h, then cooled to room temperature and poured into ice water. Excess NaOH was added to the mixture to neutralize the excess fuming sulfuric acid to pH (7-8), during titration; the reaction mixture was kept cold to avoid the nucleophilic attack on the aromatic halide by hydroxide ion. NaCl was added to precipitate the sulfonated monomer. The sulfonated monomer was then filtered and dried in an ambient condition. The sulfonated monomer was then re-crystallized three times using a mixture of alcohol as a solvent (methanol, ethanol and isopropanol) and water.

Re-Crystallization of Produced Sodium Sulfonate Monomer: Sulfonated monomer (sodium 5, 5'-carbonylbis (2-fluorobenzene-sulfonate)) is moderately soluble at room temperature in used alcohol and readily soluble in water. Both ethanol and isopropyl alcohol has proved to be desirable alternatives to methanol and provide pure, fine



Scheme 1: Synthesizing the sodium sulfonate monomer salt.

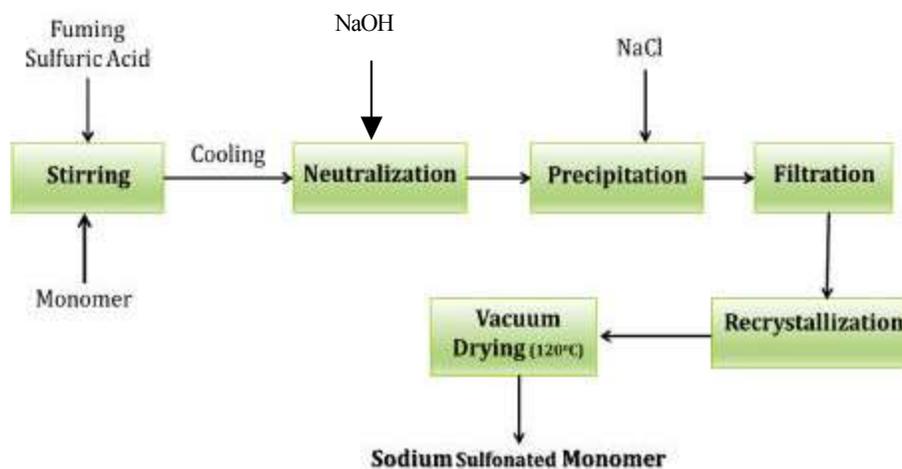


Fig. 1: Synthesis of sodium sulfonate monomer salt process flowchart.

needle like crystal [9]. Water still necessary to ensure removal of residual sodium chloride and sodium sulfate in the product since inorganic sodium salts is not appreciably soluble in alcohols. The crude product was dissolve in the minimum amount of hot (alcohol: water) mixture with different ratios until the solution becomes cloudy while keeping the mixture warm. Add a few drops of the solvent mixture to the cloudy solution until it becomes clear and then the hot mixture was filtrated by vacuum filtration. The desirable product should be observed of sulfonated monomer sodium 5, 5'-carbonylbis (2-fluorobenzene-sulfonate) crystallizing out of the solution after cooling the filtrate. Crystals were isolated by vacuum filtration; then rinsing the crystals on filter paper with the used solvent alcohol. Effect of solvent (methanol, ethanol and iso-propanol) used in recrystallization is studied on the % recovery of pure sulfonated desirable product.

RESULTS AND DISCUSSION

Sodium Sulfonate Organic Salt Synthesis and Characterization: Sulfonation is an aromatic electrophilic reaction. The choice of sulfonating agents and the chemical structure of the product depends on the substituent at the phenyl ring. Electron-donating substituent will favor the reaction whereas electron-withdrawing groups will not. 4, 4'-difluorobenzophenone has 2 electron-withdrawing groups at each phenyl ring. Therefore, a powerful sulfonation agent, fuming sulfuric acid (20% SO_3) and a relative high temperature (110°C), were chosen in the sulfonation reaction. On the basis of the electronic theory of orientation in electrophilic aromatic substitution, fluoro is an o, p-orienting group, whereas carbonyl is an m-orienting group. So the product of the sulfonation reaction is expected to be compound 1, i.e., the substitution occurred preferentially on the position that is ortho to fluoro and meta to the carbonyl group. The chemical structure of sodium 5, 5'-carbonylbis (2-fluorobenzene-sulfonate) was confirmed by Fourier transform infrared (FTIR) and ^1H NMR spectroscopy as shown in Fig. 3, 4. The FTIR spectrum (KBr substrate, cm^{-1}) shows intense absorption bands at 1664 ($\text{C}=\text{O}$ stretching), 1259 and 1093 (asymmetric and symmetric stretching vibrations of sodium sulfonate groups) and 624 (stretching vibrations of $\text{C}=\text{S}$). The ^1H NMR spectrum (500 MHz, using DMSO as a solvent) shows peaks at $\delta\text{H}5 = 8.0$ ppm, $\delta\text{H}3 = 7.8$ ppm, $\delta\text{H}2 = 7.3$

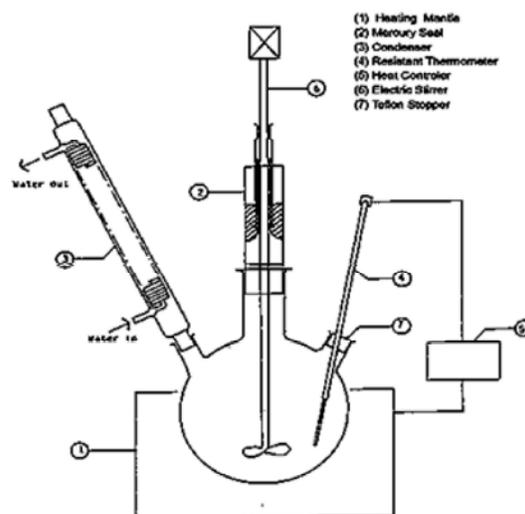


Fig. 2: Bench scale reactor for sulfonated monomer synthesis.

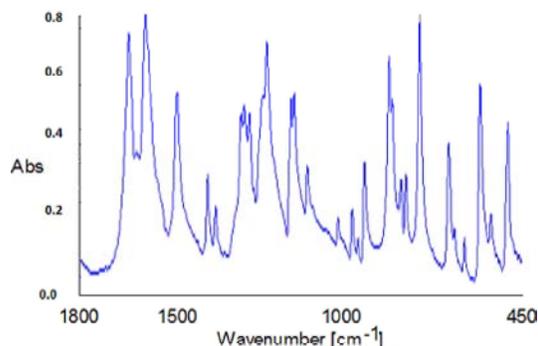


Fig. 3: FTIR spectrum of Sodium Sulfonate organic salt.

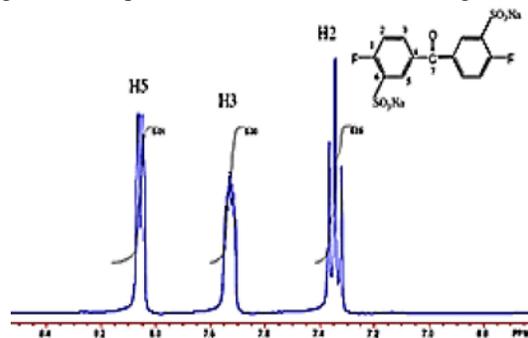


Fig. 4: ^1H NMR spectrum Sodium Sulfonate organic salt.

ppm, where H1, H2 and H3, respectively, represent the hydrogen atoms of the sulfonated monomer illustrated in Scheme 1. The spectroscopic results, which are similar to those obtained by Wang *et al.* [10] Vetter *et al.* [11] and Mohd Norddin *et al.* [12]; confirm the formation of the sulfonated monomer (sodium 5, 5'-carbonylbis 2-fluorobenzene-sulfonate).

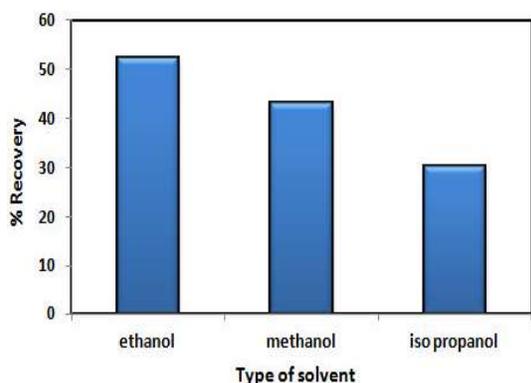


Fig. 5: Effect of solvent type on percent recovery of sulfonated monomer.

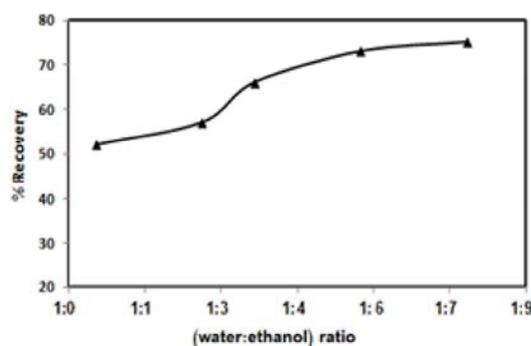


Fig. 6: Effect of (water: ethanol) ratio on percent recovery of sulfonated monomer.

Re-Crystallization of Produced Sodium Sulfonated Monomer: The effect of used solvent for recrystallization on the percent recovery of pure product of sodium 5, 5'-carbonylbis (2-fluorobenzene-sulfonate) for a recrystallization stage is calculated by the following equation:

$$\% \text{Recovery} = \frac{\text{Weight of produced compound}}{\text{Weight of crude compound started with}} \times 100$$

The sulfonated monomer is soluble in hot alcohol, also soluble in water at room temperature. Undesirable salts (impurities) such as NaCl, Na₂SO₄ are sparingly soluble in chosen alcohol (ethanol, methanol and isopropanol) (Fig.5) represents the change of the alcohol type for ratio of water: alcohol of 1:1. Despite of the higher polarity of methanol than ethanol, ethyl alcohol gave the highest percent recovery of the produced sulfonated monomer compound in the first recrystallization stage. That is due to the more solubility of impurities in methanol than in ethanol. By changing the ethanol: water ratio for studying the optimum ratio for the percent recovery it was

found that the recovery increased by increasing the ratio of ethanol to water and the maximum yield was 88 % by using (1:6) water: ethanol as illustrated in the Fig. 6.

CONCLUSIONS

Successful synthesis of 5, 5'-carbonylbis (2-fluorobenzene-sulfonate) monomer was achieved with high purity. A powerful sulfonation agent, fuming sulfuric acid (20% SO₃) and a relative high temperature (110°C), were chosen in the sulfonation reaction. The structures were confirmed by both proton NMR and FTIR. Ethanol gave the highest percent recovery of the produced sulfonated organic compound. Percent recovery was found that the recovery increased by increasing the ratio of ethanol in the solvent mixture and the maximum yield was 88 % by using (6:1) ethanol: water.

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