PRODUCTION AND CHARACTERIZATION OF SULFONATED CHITOSAN-CALCIUM OXIDE COMPOSITE MEMBRANE AS A PROTON EXCHANGE FUEL CELL MEMBRANE

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ABSTRACT

The present communication reports the preparation of a sulfonated chitosan-calcium oxide (CaO) composite membrane to be used as a fuel cell proton exchange membrane. CaO addition 0, 10, 15, 20, 25 and 30 %. Production of membranes was done by mixing dope of a chitosan solution is doped with CaO powder of varying concentration (0 %, 10 %, 15 %, 20 %, 25 % and 30 %). The crosslinking process is carried out with the participation of 0.005 % glutaraldehyde, while the sulfonation proceeds in 0.72 N H$_2$SO$_4$. The membrane’s ionic and swelling capacity is determined, the functional groups present are identified by FTIR, while the membrane morphology is elucidated by SEM. Methanol permeability and proton conductivity tests are also carried out. The optimal production of sulfonation chitosan-calcium oxide composite membrane at the addition The optimum characteristics obtained in presence of 25 % CaO refer to ionic exchange capacity of 1.517 meq/g, swelling of 28.207 %, methanol permeability of 1.211 x 10$^{-4}$ kg/m$^2$s, and proton conductivity of 6.415 x 10$^{-5}$ S/cm.

Keywords: chitosan, CaO, membrane, fuel cell.

INTRODUCTION

The development of a fuel cell using a renewable material is very important to reduce dependency on fossil energy resources which are already scarce. The fuel cell is an electrochemical device that consists of electrodes (an anode and a cathode) and an electrolyte. It usually produces electricity from a hydrogen fuel and an oxidant [1]. This is done continuously when the external fuel supply is available. Fuel cells need to be developed because of their energy efficiency compared to that of the conventional power generation, their environmental friendliness (SO$_x$ and NO$_x$ emissions are very low) and fuel tolerance [2].

The Proton Exchange Membrane Fuel Cell (PEMFC) has many advantages such as low operating temperature, low cost, and suitability for discontinuous operation [3]. The commercially used PEM refer to polytetrafluoroethylene (PTFE) one with a sulfonate group of a branched chain. Its trade name is Nafion. It is known as an efficient membrane as it can hold and deliver protonated H$_2$ gas [4]. However, Nafion has drawbacks, namely high methanol crossover and high manufacturing costs [5]. Therefore, Nafion has to be replaced by a material providing low methanol crossover, high proton conductivity, high durability and low cost production.

Chitosan is a Nafion substitute which originates from seafood waste or natural and economical polymers. Chitosan results from deacetylation of chitin, a substance found in the body frame of bracket crustaceans and fungal cell wall. Chitosan can function well as a polymer
electrolyte membrane and as a material for ion-solvating composite polymer membrane. The advantages of chitosan as a polymer electrolyte membrane refer to: (1) its low price and environmental friendliness; (2) its low methanol permeability; (3) presence of OH and NH functional groups which can be chemically modified aiming specific properties [6]. Chitosan can be used as a membrane fuel cell because it has conductivity level of $3.87 \times 10^{-2} \text{ S cm}^{-1}$ [7]. But chitosan has a poor thermal stability like other natural polymers which are not resistant at temperatures above 100°C. Thus, chitosan needs crosslinking like other inorganic materials as zeolite A, bentonite and calcium oxide. This results in its mechanical properties improvement. Furthermore, the ion exchange capacity in absence of a crosslinker is 2.50 meq g$^{-1}$, while that in presence of $\text{H}_2\text{SO}_4$ as a crosslinker increases to 5.66 meq g$^{-1}$ [6].

CaO has a low absorption capacity in respect to methanol, therefore, composites containing CaO can be used as a substitute for Nafion. CaO composites have good proton transportation resistance because their proton conductivity is lower than that of Nafion. According to Mat and Liong [8] the proton conductivity the matrix chitosan-PVA-CaO membrane decreases from 0.038 S cm$^{-1}$ to 0.001 S cm$^{-1}$ because of the low absorption of water. CaO when present in a high concentration can provide agglomeration which in turn disrupts proton conductivity. But the diffusion coefficient increases with CaO concentration increase from $5.19 \times 10^{-7} \text{ cm}^2 \text{s}^{-1}$ to $8.49 \times 10^{-7} \text{ cm}^2 \text{s}^{-1}$. This compound can also be added to ZrO$_2$ for SOFC application. The study of Wafiroh [9] shows that the conductivity of chitosan increases to 0.0023 S cm$^{-1}$ in case of hybridization with bentonite. Furthermore, the proton conductivity of sulfonated zeolite A hybrid chitosan is $2.2 \times 10^{-4} \text{ S cm}^{-1}$, while that of bentonite hybrid chitosan amounts to $4.86 \times 10^{-4} \text{ S cm}^{-1}$.

The results referring to the low proton conductivity of chitosan crosslinked with CaO show that it has to be increased. Sulfonation is a method which can be applied. There is an investigation [10] on a chitosan membrane crosslinked with glutaraldehyde and $\text{H}_2\text{SO}_4$. The proton conductivity obtained in this case amounts to $0.024 \text{ S cm}^{-1}$, while the proton permeability is found equal to $7.3 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$.

Based on the considerations presented above this research focuses on the preparation of sulfonated chitosan-CaO composite membranes with varied addition of CaO 0 %, 10 %, 15 %, 20 %, 25 % and 30 % (w/w) to commercial chitosan as the main ingredient and glutaraldehyde and sulfuric acid. The membranes prepared will be characterized by SEM and FTIR. The ion exchange capacity, the swelling and the methanol permeability will be determined. The performance of the membrane in terms of its proton conductivity will be tested with the application of the method of electrochemical impedance spectroscopy.

**EXPERIMENTAL**

Analytical grade calcium oxide (CaO; Merck; 99 %), sodium hydroxide (NaOH; Merck; 99 %), glacial acetic acid (CH$_3$COOH; Merck; 100 %), sulfuric acid (H$_2$SO$_4$; Merck; 98 %), glutaraldehyde (CH$_2$($\text{CH}_2\text{CHO}$)$_2$; 25 %; Merck), distilled water, demineralized water, phenolphthalein indicator, methanol (CH$_3$OH; Sigma Aldrich; 99.8 %), and chitosan from CV Ocean Fresh were used without further purification.

The membrane investigated was obtained by dissolving 1.5 g of chitosan in 80 mL of 2 % (w/w) solution of acetic acid. CaO was added in an amount of 10 % (w/w) in respect to the total weight of chitosan. Then the mixture was stirred for 6 hours in room temperature. Subsequently it was left to stand overnight to eliminate the bubbles on the surface. After that, the solution was poured on a petri dish and heated on a hot plate at a temperature of 45°C. The same procedure was applied in case of adding CaO of a concentration of 0 %, 15 %, 20 %, 25 % and 30 % (w/w). All membranes produced were dried, soaked in 4 % (w/v) solution of NaOH, washed again with distilled water, and finally dried. Then the membranes were crosslinked with 0.005 % (v/v) solution of glutaraldehyde through soaking in room temperature for 40 min. The membranes were dried prior to the sulfonation process. The latter was carried out by immersing each membrane in 0.72 N solution of $\text{H}_2\text{SO}_4$ for 1 h. Then the membrane treated was neutralized to a neutral pH value, washed with demineralized water, checked with a blue litmus paper and then dried [10]. Then a tensile, ion exchange capacity
and swelling tests were carried out. The membrane of optimal mechanical properties was identified. It was then subjected to FTIR and SEM analysis. Its methanol permeability and proton conductivity were identified.

RESULTS AND DISCUSSION

The sulfonated chitosan-CaO composite membrane of the optimal mechanical properties is selected based on some criteria such as: high values of the stress testing and Young modulus, low swelling and high ion exchange capacity. It is found that this is the membrane containing 25 % of CaO. It shows a Young modulus value of 0.133 kN/cm$^2$, ion exchange capacity of 1.517 meq g$^{-1}$, and swelling value of 28.207 %. It is worth adding that Nafion 117 has an ion exchange capacity of 0.91 meq g$^{-1}$ [2] and swelling by 33.3 % [10].

The functional groups present in the membrane subjected to further investigation are determined by FTIR. The test is performed in the wave number range of 4000 cm$^{-1}$ - 400 cm$^{-1}$ (mid-infrared region). The upper limit is determined by CaO peak wave number which is 400 cm$^{-1}$. The spectrum obtained shows a peak at 3356.14 cm$^{-1}$ referred to the hydroxyl functional groups of chitosan, the amide I and amide II peaks at 1589.34 cm$^{-1}$, the peak of the chitosan amide carbonyl bond 1635.64 cm$^{-1}$. The spectrum indicates also the presence of CaO group within wave numbers of 432.05 cm$^{-1}$ and 455.2 cm$^{-1}$ and a hydrogen bonds between NH$_3^+$ (of chitosan) and O (of CaO) at 995.27 cm$^{-1}$. There is a peak at 1651.07 cm$^{-1}$ which is indicative of the group (-C = N-). The latter results from

![Chemical structure](image)

Fig. 1. Hypothesis reaction for the formation of sulfonated chitosan-CaO composite membrane.
the bond of chitosan-CaO with glutaraldehyde crosslink. The peak at 1535.34 cm$^{-1}$ shows the presence of symmetric $\text{-NH}_3^+$ obtained chitosan-CaO-glutaraldehyde bonding with H$_2$SO$_4$. The vibration of S = O is recorded at 1095.57 cm$^{-1}$.

The assumed interaction between chitosan, CaO, glutaraldehyde, and H$_2$SO$_4$ is presented in Fig. 1. Hydrogen bonds are formed between O (as O$^-$) of CaO and $\text{-NH}_2$ (as $\text{-NH}_3^+$) of chitosan in correspondence with the findings of Smitha et al. [10]. The protonated chitosan amide group is bonded to glutaraldehyde in the course of crosslinking. Furthermore, covalent bonds (-C = N-) are formed between $\text{-NH}_2$ of chitosan and -CHO of glutaraldehyde. Ionic bonds appear as a result of the process of sulfonation. They connect the anionic sulfonate group and the cationic chitosan amide group ($\text{-NH}_3^+$) [10].

The morphology of the membrane investigated is identified by SEM. In fact, the structure of the surface and the cross section, as well as the size of the pores is determined with a resolution of 1 μm or 1000 nm. The results obtained are shown in Fig. 2 using a magnification of 15,000 times. It is evident that the membrane studied has pores on the surface and at the cross-section. It can be seen that the pores spread evenly though the pore size is still relatively small - its value equals on the average to 1021.3 nm on the surface (a) and to 502 nm at the cross-section (b). The results reported in ref. [8] show that chitosan-PVA composite containing 20 % of CaO has no pores because of CaO particles agglomeration in the matrix of chitosan-PVA. This results in the composite membrane semi-homogenous solubility in Chitosan - PVA.

The membrane investigated is tested as a fuel cell proton exchange membrane. Its methanol permeability and proton conductivity are tested. The methanol permeability test is conducted using a dead-end tool with unpressured stirring. It is found that the methanol permeability is equal to 1.221 x 10^{-4} kg/m$^2$h or 0.439 kg/m$^2$h. The test results show that CaO composite of chitosan treated with glutaraldehyde-sulfonation crosslink exceeds nafion in restraining methanol as the methanol permeate flux rate value of nafion amounts to 1.30 kg/m$^2$h [11, 13].

The proton conductivity of the membrane studied is equal to 6.415 x 10^{-5} S/cm. The value is lower than that of nafion 117, which reaches 0.086 S/cm [2]. However, it is higher than the value of chitosan, which is found equal to 3.87 x 10^{-7} S/cm [7]. The proton conductivity pointed above is insignificant due to the presence of CaO, which amounts only to 25 % (w/w) of the total chitosan [8]. In addition, the concentration of sulfuric acid used and the processing time for membrane sulfonation is too short so that the sulfonate groups crosslinked with chitosan are relatively few. This is in correspondence with the theoretical considerations presented in ref. [6]. It is pointed out there that the number of the crosslinked groups is affected by the crosslinker concentration, the length of the crosslinking process, and the temperature.
applied. The interpretation presented is also consistent with the research conducted by Handayani et al. [12]. It is found there that the material proton conductivity increases with increase of the temperature of the crosslinking process.

**CONCLUSIONS**

Sulfonated chitosan-CaO composite membranes can be made by mixing chitosan and CaO powder followed by crosslinking with glutaraldehyde and H₂SO₄. Optimum mechanical properties are shown by the membrane containing 25% of CaO. They refer to Young modulus value of 0.113 kN/cm², ion exchange capacity of 1.517 mₑq/g, and swelling of 28.207%. The membrane investigated can be effectively used as a proton exchange membrane in a fuel cell because the methanol permeability and the swelling obtained exceed those of nafion.

**REFERENCES**