Composite chitosan and quaternary ammonium modified nanofibrillar cellulose anion exchange membranes for direct ethanol fuel cell applications

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Abstract. Fuel cells are a promising technology for energy production, but their commercialization is hindered mainly due to high costs. Direct alkaline ethanol fuel cells (DAFC) are receiving increasing attention as they can utilize cheaper, non-precious metal catalysts. A vital component of a DAFC is the anion exchange membrane (AEM). Currently, the commercially available AEMs don't possess satisfactory properties. This indicates a need for the development of new highly efficient, environmentally friendly, and economically viable AEMs. Synthesis of synthetic polymer AEMs is usually complex and time-consuming, as well as environmentally unfriendly. Therefore, it is highly desired that the membrane material is bio-renewable, non-toxic and environmentally benign. In this work, a series of biopolymer membranes were designed by a simple, cost-effective, dispersion-casting procedure, fully complying with green-chemistry principles. Design of experiments was used as a methodology for identifying optimal combinations of influencing factors and their relations within selected responses. The obtained chitosan-Mg(OH)$_2$ composite membranes containing modified nanofibrillar cellulose (CNF) fillers with quaternary ammonium groups were investigated for their mechanical properties, swelling ratio, ethanol permeability and ion exchange properties. Obtained data suggest the applicability of newly prepared, biopolymeric composites as eco-friendly AEMs in DAFC technologies.

1 Introduction

Among the most significant societal challenges nowadays are CO_2 emissions and global warming, so a lot of attention is directed towards the use of alternative energy sources. To this end, much of the research focus has been aimed at fuel cells, electrochemical devices that can be used for alternative energy production. It is a device that uses fuel and an oxidant to produce electrical energy through an electrochemical reaction. [1] Similar to batteries, which power portable devices and electrical vehicles, also fuel cells convert chemical energy into electrical energy. There are many different types of fuel cells, but all of them have the same basic structure: two electrodes and an electrolyte between them. They are mainly differentiated by the type of electrolyte, which is responsible for ion transport, and by the operating temperature. A fuel cell with a polymer electrolyte (PEFC) can operate in an acidic or alkaline environment, depending on the properties of the polymer. A PEFC with an anion exchange membrane (AEM) operating in alkaline conditions has benefits in comparison to a PEFC operating in acidic conditions, as the OH$^-$ anions pass through the AEM in the opposite direction as fuel. In addition, cheaper non-noble catalysts can be used. [2] The basic structure of AEMs for alkaline fuel cell applications is a hydrophobic polymer backbone with added positively

charged hydrophilic functional groups, one of them being the quaternary ammonium group, which is permanently positively charged. AEMs need to have a high ion conductivity, be mechanically stable and have a low ethanol permeability as well as good stability in an alkaline environment. [3]

Biopolymer-based membranes are renewable and eco-friendly alternatives to synthetic membranes, offering a reasonable cost/effectiveness ratio. [4] Chitosan membranes have already been included in different fuel cell set-ups, including alkaline anion exchange membrane fuel cells (AAEMFCs). [5] Chitosan is a low-cost non-toxic biopolymer with high chemical stability, which can readily form films. Chitosan membranes on their own do not possess appropriate mechanical properties and conductivity properties; therefore, the introduction of fillers can be beneficial to improve those properties. [1] Nanofibrillar cellulose (CNF) is a biomaterial with a high aspect ratio and has the potential to improve the chitosan membrane's shortcomings, such as mechanical stability. Additionally, CNF can be readily modified on the abundant -OH groups, thus formulating the positively charged fillers, which can improve the conductive properties of the AEM.

Herein we report the preparation of composite chitosan membranes with (modified) CNF fillers for the

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application of AEMs in AAEMFCs. The properties of resultant nanocomposites relevant for AEM applications were investigated, in terms of tensile strength, EtOH fuel permeability, swelling ratio, and ion exchange capacity.

2 Methods

2.1. Membrane production

Chitosan-Mg(OH)$_2$ dispersion was used as a base for composite membrane preparation. The membranes have been prepared similarly as described in our previous work [3]. Chitosan was dissolved in Mili-Q water by adjusting the pH to 2.0 (with 1M HCl) at room temperature under stirring. The solution was stirred overnight until a transparent homogenous solution was obtained. Next, 1 wt.% Mg(OH)$_2$ dispersion was added until a pH value of 6.0 – 6.2 had been reached, and the dispersion was diluted to a final 1.wt.% of chitosan. Design of Experiments was used to determine the relations between different membrane production factors and membrane properties in order to obtain appropriate AEM properties for fuel cell applications (low fuel permeability, high ion conductivity, etc.). The experimental design consisted of 17 membranes with different contents of modified or unmodified fillers. Membranes with a modified filler (CNF polyDADMAC) content from 0 – 0.125 g and unmodified filler (CNF) content from 0 – 0.375 g were prepared. The resulting dispersions have been cast as membranes and dried at different temperatures. When dry, the membranes were neutralized with 1 M NaOH and subsequently washed with Mili-Q water and left to air dry. The modified fillers were obtained by adsorption between CNF and polydiallyldimethylammonium chloride (polyDADMAC) under vigorous stirring. The resulting CNF polyDADMAC was washed with Mili-Q water.

2.2 Zeta potential

The zeta potential of monodispersed CNF and CNF polyDADMAC particles in water dispersion with a concentration of 0.001 wt.% was obtained as streaming potential in a DLS apparatus at different pH values set by 0.1 M NaOH or 0.1 M HCl.

2.3 Ethanol permeability

Ethanol (EtOH) permeability through CS nanocomposite membranes has been measured in temperature-controlled diffusion cells at 25 °C ± 1 °C. [6], [3] The diffusion cell consisted of two glass compartments (source and receiving compartment), each 25 ml in volume, and the membrane sample separating the two compartments in between. Before each experiment, the membrane was equilibrated in Mili-Q water for 24 h. The source compartment was filled with 25 ml of 2 M EtOH in 6 M KOH solution (i.e., 8.5 w/w % EtOH), and the receiving compartment was filled with 25 ml of 6 M KOH. Both compartments have been filled simultaneously in order to apply the same pressure

on the membrane from both sides. The membrane sample had an effective surface area of 7.026 cm^2. The concentration of permeated EtOH was obtained based on the conductivity measurements, measured by a conductometer, in the receiving compartment at different time intervals. The permeability coefficient of EtOH, *P* *(cm^2 s^{-1})* was calculated using the equation below.

$$P \left(\frac{cm^2}{s} \right) = \frac{(C_B - C_{B0})}{(t - t_0)} \times \frac{V_B \cdot l}{A \cdot C_{A0}} \qquad (1)$$

where C_{A0} represents the initial concentration of EtOH in the source compartment, and V_B represents the volume of KOH in the receiving compartment. A and l represent the area and thickness of the membrane, respectively.

2.4 Ion exchange capacity (IEC)

To obtain the titrated gravimetric IEC values, AEMs were weighed to determine the dry mass and then converted to the OH$^-$ form in 1 M KOH solution for 24 hours, washed with Mili-Q water, and subsequently immersed in 40 ml of 0.01 M HCl standard solution for 24 h. The solutions were then titrated with a standardized KOH (0.1 M) solution. Following the potentiometric titration, parameter IEC was calculated in terms of mili-equivalents (meq) of OH$^-$ions per gram of dry AEM from the following equation:

$$IEC \left(\frac{meq}{g} \right) = \frac{(V_{blank} - V_{membrane}) \cdot c_{HCl}}{m_{dry \, membrane}} \qquad (2)$$

where V_{blank} and $V_{membrane}$ represent the consumed volumes [ml] of 0.1 M KOH solution for the blank and sample membranes, respectively. c_{HCl} represents the molar concentration [mol/l] of HCl solution, and $m_{dry \, membrane}$ represents the mass of dry membrane samples [g].

2.5 Mechanical properties

The tensile strength at maximum (MPa) of the membranes was determined by Shimadzu, AG-X plus 10 kN electromechanical universal testing machine. Membrane samples with specimen dimensions: 10 mm × 20 mm were vertically mounted. Application of tensile force proceeded at 5 mm min^{-1}. Three specimens were tested per sample and average values and standard deviations were calculated. Prior to testing, membrane samples were equilibrated in liquid water and ambient air at room temperature for 3 h.

2.6 Swelling ratio

Swelling ratio measurements were performed in 6 M KOH at 60 °C. Membrane samples with dimensions of 1 × 1 cm^2 (A_{dry}) were immersed in an alkaline medium (6 M KOH at 60 °C.) After immersion, the surplus alkaline solution on the membrane surface was removed with a paper towel, and then the surface area (A_{wet}) of the wet membranes was determined at room temperature after 24 hours. In-plane swelling ratio (SR) of the membranes has been determined

after 24 hours when equilibrium was reached from the following equation.

$$SR_{In-plane} = \frac{A_{wet} - A_{dry}}{A_{dry}} \cdot 100\ \% \qquad (3)$$

3 Results

Figure 1 shows the zeta potential of CNF and CNF polyDADMAC dispersion which were used as a filler in the composite chitosan membranes. The successful modification of CNF by the reagent polyDADMAC was observed as an obtained positive zeta potential value on the purified product. A positive zeta potential correlates to a positive charge but not also to the quantity of charge. The neat CNF dispersion shows a negative zeta potential in all pH ranges except for pH 2, where it is close to zero, therefore differentiating in charge from the modified CNF. The opaque appearance of the resulting composite chitosan membrane with CNF fillers is shown in Figure 2.
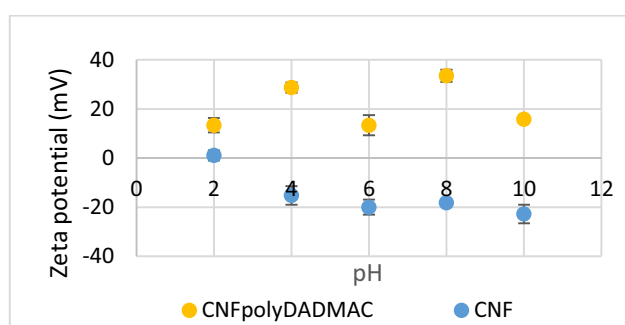

Fig. 1. Zeta potential of modified and un-modified fillers

Fig. 2. Composite chitosan CNF membrane

Fuel permeability is an undesirable property as a high membrane fuel permeability can lead to a decreased fuel cell performance. Fuel permeability expressed as EtOH permeability of the composite membranes is shown in Figure 3. A higher amount of unmodified filler increases the EtOH permeability in comparison to a chitosan membrane without fillers. In contrast, with the addition of modified CNF polyDADMAC fillers, EtOH permeability is decreased in comparison to a pure chitosan membrane. Fuel permeability in membranes is linked to different factors, and the 3D structure of the membrane with formed channels and clusters has a huge role on the permeability. The addition of un-modified un-charged CNF fillers can result in a bigger chain spacing between chitosan chains,

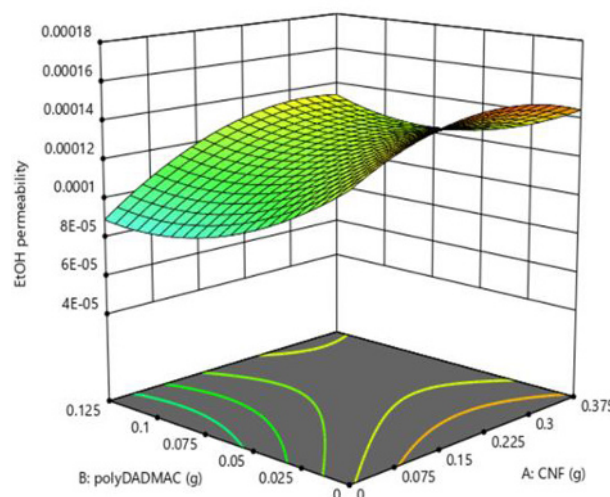and the charged modified CNF fillers can diminish the effect.

Fig. 3. EtOH permeability of membranes with different filler contents

Ion exchange capacity (IEC) corresponds to the ion exchangeable groups present in the membrane. IEC calculated from titration measurements of the composite membranes is shown in Figure 4. With the introduction of unmodified fillers, IEC significantly decreased in comparison to a pure chitosan membrane; however, the inclusion of modified fillers caused only a minor decrease in IEC. The highest amount of modified filler had a similar IEC to a membrane without fillers.
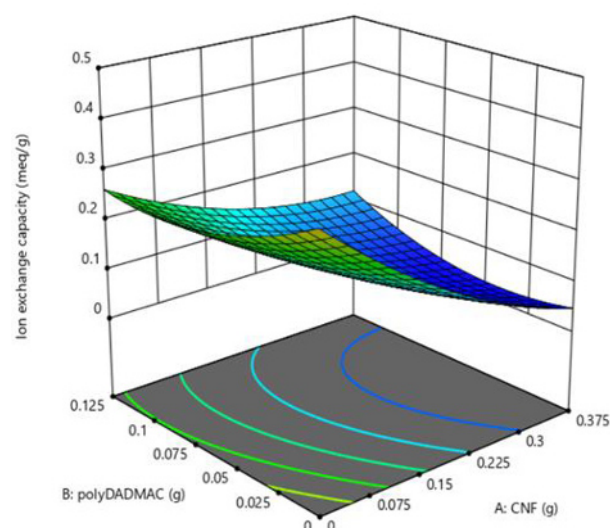

Fig. 4. Ion exchange capacity of membranes with different filler contents.

The mechanical properties of the composite membranes were determined by a tensile strength test. Results of the tensile strength tests of the composite membranes are shown in Figure 5. The tensile strength is greatly improved with the addition of a higher amount of filler. The greatest improvement in tensile strength is seen for the membranes with the highest loading of unmodified and modified CNF fillers, which is directly related to the excellent mechanical and physical properties of CNF.
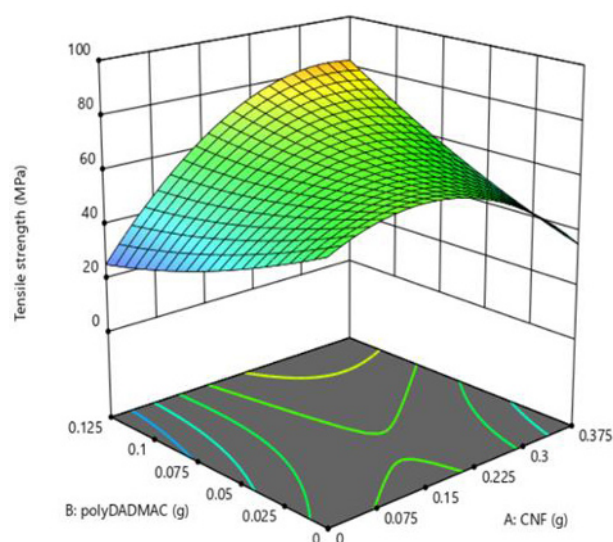
Fig. 5. Tensile strength of membranes with different filler contents.

The in-plane swelling of the membranes might loosen the contact between current collectors and membrane electrode assembly in the fuel cell. In-plane swelling ratio (SR) of the composite membranes is shown in Figure 6. The SR was decreased with the presence of unmodified and modified CNF fillers, making the inclusion of both types of fillers beneficial in the composite chitosan AEMs. The highest amount of un-modified and modified fillers resulted in the lowest SR.
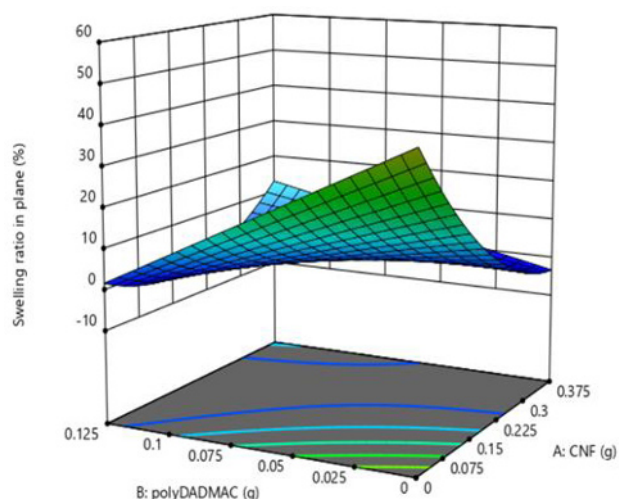
Fig. 6. In-plane swelling ratio of membranes with different filler contents.

4 Conclusions

A series of composite chitosan membranes with different amounts of unmodified and modified CNF fillers were prepared by a simple dispersion casting technique. The inclusion of fillers enables the tuning of membrane properties for AAEMFC applications. The lowest EtOH permeability of $8.97 \cdot 10^{-5}$ cm^2/s and in-plane swelling ratio of 1.78 % was observed for the chitosan membranes with the highest amount of CNF polyDADMAC. The highest IEC of 0.35 meq/g was observed for the chitosan

membrane. Tensile strength of the highest CNF and CNF polyDADMAC filler loading in the composite chitosan membrane corresponded to 82.36 MPa. In comparison, in a product sheet for a commercially available proton exchange membrane Nafion™ 117 [7] it can be found that the commercial membrane has almost a half lower tensile strength (43 MPa) and a higher (10%) in-plane swelling ratio and a commercial AEM fumasep® FAA-3-50 [8] also has a lower tensile strength (25-40MPa) and has a comparable swelling (0-2%); although testing should be done in the same conditions to offer a reliable comparison. The results demonstrate that the obtained membranes are promising AEM candidates for alkaline alcohol fuel cell applications. Additionally, cell tests will need to be performed to showcase the AEMs behaviour in actual fuel cell set-ups.

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