



# Fabrication and Characterization of Chitosan Nanoparticle-Incorporated Quaternized Poly(Vinyl Alcohol) Composite Membranes as Solid Electrolytes for Direct Methanol Alkaline Fuel Cells



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## ABSTRACT

In this study, we designed a method for the preparation of chitosan nanoparticles incorporated into a quaternized poly(vinyl alcohol) (QPVA) matrix for direct methanol alkaline fuel cells (DMAFCs). The structural and morphological properties of the prepared nanocomposites were studied using X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscope (TEM) and dynamic laser-light scattering (DLS). The crystallinity of the nanocomposite solid electrolytes containing 0 and 10% chitosan nanoparticles were investigated using differential scanning calorimetry (DSC). The electrochemical measurement of resulting nanocomposite membranes were analyzed according to the following parameters: methanol permeability, liquid uptakes, ionic conductivity and cell performances. The composite membranes with 10% chitosan nanoparticles in a QPVA matrix (CQPVA) show suppressed methanol permeability and higher ionic conductivity than pristine QPVA. In addition, the glutaraldehyde cross-linked nanocomposite film exhibited improvement on the methanol barrier property at 80 °C. The peak power density of the DMAFCs reached 67 mW cm<sup>-2</sup> when fed into 1 M of methanol in 6 M of KOH.

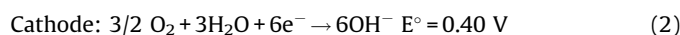
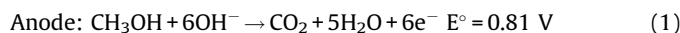
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## 1. Introduction

In recent years, direct methanol fuel cells (DMFCs) have attracted significant attention as alternative energy sources due to their advantages of easy transport, small footprint, light weight, lower CO<sub>2</sub> emission and more environmentally friendly compared to traditional fossil fuel systems. For DMFCs, methanol is used as fuel because it exhibits a high power density characteristic as a potential source of energy [1]. The proton-exchange membrane is an important component in DMFCs with respect to improvement of cell performance via an increase in conductivity and a reduction of permeability [2]. However, the commercial Nafion proton-conducting membrane still has the drawback of high methanol crossover through the membrane electrolyte, which leads to an

offset of the cell potential and poisoning of the Pt cathode catalyst via the formation of CO [3]. Thus, it is important to perform research on alternative proton exchange membranes.

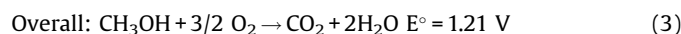
In DMFCs, the oxygen reduction reaction occurs at the cathode, which creates two problems that have hampered their use in applications: corrosive materials in acidic environments and slow reaction kinetics [4,5]. The development of DMAFCs is being pursued to overcome these problems. The working principle of DMAFCs involves a methanol and alkali solution fed into the anode, which react with the catalyst to produce carbon dioxide, water and electrons (the half-reaction is shown in Eq. (1)). The electrons travel via an external circuit and then react with humidified oxygen to induce hydroxyl ions, as shown in Eq. (2). The overall combustion reaction of the methanol and oxygen is described in Eq. (3), where E° is the standard potential at 298.15 K and at a pressure of 1 bar [6].



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In DMAFCs, the methanol oxidation rate is faster in alkaline media than in acidic solution, which reduces the phenomenon of poisoning and corrosion. In addition, the OH<sup>-</sup> anion transportation direction helps to reduce methanol crossover [7]. The water molecules are produced at the anode, which enables easy water management [8]. Less expensive non-platinum catalysts can be used on both electrodes, which provides a cost reduction advantage.

Recently, designing an excellent conductive electrolyte is an emerging field; more specifically, a membrane that selectively transports hydroxide (OH<sup>-</sup>) ions is essential for DMAFCs. Alkaline-doped polymer films are considered for use as potential electrolytes due to their benefits of being inexpensive, highly conductive and easy to fabricate. In addition, many researchers are working to optimize the conductivity and methanol permeability of polymer membranes used in DMAFCs. Many inorganic filler materials are found to enhance the mechanical properties of membranes. The KOH-doped poly(vinyl alcohol) (PVA)/TiO<sub>2</sub> and PVA/Q-SiO<sub>2</sub> composite electrolytes have reached maximum power density ( $P_{\text{max}}$ ) values of 7.54 mW cm<sup>-2</sup> and 35.13 mW cm<sup>-2</sup> at 60 °C and 50 °C, respectively, in DMAFCs [9,10]. In our previous report, the PVA containing 20% fumed silica nanoparticles was used as a solid electrolyte, and the nanofiber incorporation reduced the polymer crystallinity, enlarged the free volume and enhanced the water diffusivity [7]. In addition, carbon nanotubes (CNTs) and Fe<sub>2</sub>O<sub>3</sub>-CNTs modified PVA composites were reported to reduce the methanol permeability and increase the ionic conductivity, the  $P_{\text{max}}$  values of their DMAFCs were 39 mW cm<sup>-2</sup> and 87.8 mW cm<sup>-2</sup> at 60 °C, respectively [11,12]. The results indicate that incorporation of micro- or nano-sized fillers into a PVA matrix resulted in lower methanol permeability and enhanced the application of DAMFCs.

However, the KOH doped in PVA film may be easily washed away if water or diluted KOH solution contacts the PVA membrane [13]. Fixed charges on the polymer backbone are beneficial to improve the conductivity of the polymer electrolyte. Xiong et al. reported that quaternary ammonium groups are good charge carriers when grafted onto the PVA matrix, and the ionic conductivity of the quaternized polyvinyl alcohol (QPVA) membranes can be as high as  $7.34 \times 10^{-3} \text{ S cm}^{-1}$  at 30 °C [14]. Yang et al. used QPVA with 10% Al<sub>2</sub>O<sub>3</sub> to form a nanocomposite membrane for DMAFCs, with a  $P_{\text{max}}$  of 36.15 mW cm<sup>-2</sup> obtained in a DMAFC at 25 °C [15]. To improve the ionic conductivity and cell performance, chitosan was chosen as the nanofiller due to its high mechanical strength, low relative humidity, low cost and non-toxic nature [16]. The bulk chitosan was reduced to nanoparticles that enable hydrophilic nanofillers in polymeric matrix for ion-solvating polymer electrolytes membrane to improve ionic conductivity, thermal stability, and fuel cell performance [17]. The chitosan nanoparticle backbone makes it possible to tailor the physico-chemical properties that allow chemical modification using certain functional groups [18]. The chitosan amine and hydroxyl groups have good adsorption properties and act as an important additive in the filtration process, providing desirable alcohol barrier properties via cross-linking [19,20]. Zhang et al. fabricated polyvinyl alcohol/chitosan blending composites as proton-conducting membranes and found high levels of water uptake, but they were always accompanied by swelling problems; these membranes were found to have the conductivity of 0.0006 S cm<sup>-1</sup> [21]. Several literature reports also suggest that the chitosan film conductivity was approximately  $10^{-2} - 10^{-4} \text{ S cm}^{-1}$  [22,23]. Therefore, the use of an organic filler to replace the common inorganic materials enhances the conductivity via the

functional groups and also improves the effect of reducing methanol permeability. Yang et al. reported PVA/chitosan blends with high conductivity ( $10^{-2} \text{ S cm}^{-1}$ ) and low methanol permeability ( $10^{-6} - 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ) for DMFCs applications [24]. In addition, Xiong et al. presented QAPVA/HACC blend membranes that exhibit high conductivity and low methanol permeability; however, the fuel cell performance was not verified [25]. From the available literature, the chitosan blends were incorporated into a pristine PVA matrix to study the effect of their conductivity, permeability, thermal stability and cell performance of these nanocomposite membranes in fuel cell applications. Therefore, the present work considers the incorporation of chitosan nanoparticles into a QPVA matrix to suppress the methanol permeability, improve ionic conductivity and enhance DMAFCs performance.

In this paper, we investigated chitosan nanocomposite membranes that act as a solid electrolyte for DMAFCs. The chitosan nanoparticles were synthesized using the chemical co-precipitation method with a homogenizer to decrease the particle size and enhance the degree of deacetylation. The nanoparticles were dispersed in a QPVA matrix, and then the mixtures were constructed into thin-film membranes using a solution-casting method. The effective ion-exchange capacities were increased in the chitosan-containing membrane compared with the pristine QPVA membrane. In addition, the present work highlights the importance of the cross-linking agents (glutaraldehyde) to improve the physico-chemical properties and conductivity of methanol fuel cells. The following properties of pristine and glutaraldehyde cross-linked chitosan nanocomposite membranes were investigated: structural, surface morphology, permeability, methanol uptake, KOH uptake, vapor uptake and ionic conductivity. Finally, the cell performance were measured at different temperatures and various methanol concentrations, and the performance correlation with the electrolyte characteristics was studied in detail.

## 2. Experimental

### 2.1. Materials

Chitosan, potassium hydrogen phthalate (KHP) and methanol (HPLC grade, 99.9%) were purchased from Acros Organics (Geel, Belgium). Poly(vinyl alcohol) (PVA, average molecular weight of 89000–98000), glycidtrimethyl ammonium chloride (GTMAC, 99%), acetic acid, glutaraldehyde (GA, 50% mass in water), hydrochloric acid (HCl, 37% volume in water), potassium hydroxide (KOH) and sodium hydroxide (NaOH, 50% w/v) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All the chemicals were of analytical grade and used without further purification. Gas diffusion electrodes with 6 mg cm<sup>-2</sup> Pt–Ru/C for the anode and 5 mg cm<sup>-2</sup> Pt/C for the cathode were purchased from E-tek (Somerset, NJ, USA).

### 2.2. Preparation of chitosan nanoparticles

In a typical synthesis, chitosan flakes (4 g) were dissolved in 500 mL of 0.3 M acetic acid solution by continuous magnetic stirring until the chitosan was completely dissolved. Next, 0.4 M of sodium hydroxide was dissolved in 500 mL of deionized water. The acidic chitosan solution was reduced to form chitosan suspension after the drop-wise addition of NaOH solution using a peristaltic pump (at a flow rate of 31 mL min<sup>-1</sup>) and then homogenized at a rate of 18200 rpm. The suspension solution was rinsed with deionized water until the solution became neutral. The obtained precipitated products were collected and then freeze-dried to form dry powders.

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