



Alkali doped polyvinyl alcohol/graphene electrolyte for direct methanol alkaline fuel cells



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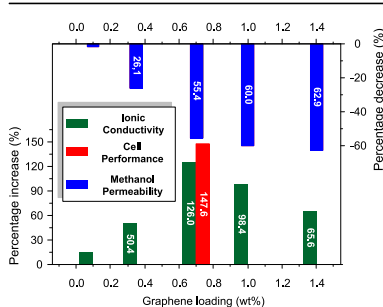
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HIGHLIGHTS

- Alkaline nanocomposites membranes prepared by simple blending process.
- Transport properties of membranes were improved with optimum graphene loadings.
- A significant enhancement of the ionic conductivity for the composite membranes.
- A graphene loading of 1.4 wt% giving a ~73% improvement in tensile strength.

GRAPHICAL ABSTRACT



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ABSTRACT

Despite the intensive effort directed at the synthesis of anion exchange membranes (AEMs) only a few studies show enhanced ionic conductivity with simultaneous suppression of unfavourable mass transport and improved thermal and mechanical properties. Here we report an alkaline nanocomposite membrane based on fully exfoliated graphene nanosheets and poly(vinyl alcohol) (PVA) prepared by a simple blending process. The composite membrane shows improved ionic transport due to the homogeneous distribution of the graphene nanosheets which are able to form continuous, well-connected ionic channels. Significant enhancement of the ionic conductivity for the prepared graphene/PVA composite membranes is observed with a 0.7 wt% graphene loading resulting in a ~126% improvement in ionic conductivity and a ~55% reduction in methanol permeability. The resulting maximum power density obtained by incorporating the membrane in a cell is increased by ~148%. A higher graphene loading (1.4 wt%) enhances the adhesion of the nanofiller–matrix, giving a ~73% improvement in the tensile strength. This study provides a simple route to designing and fabricating advanced AEMs.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are being developed as a future power generation technology with the

potential to deliver clean-at-the-point-of-use power. As well as their environmental friendliness they additionally offer high power densities, high energy conversion efficiencies, and low starting temperatures [1,2]. Although PEMFCs have been widely researched in recent decades and are considered to be an important development, their inherent limitations in acidic conditions, due to: noble metal catalyst poisoning by carbon monoxide at low temperatures, complex water management, limited PEM working lifetime and

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high fuel permeability, together with the rarity and consequent high cost of platinum catalysts bring various limitations to PEMFCs [3–5]. In contrast to acidic fuel cells, alkaline fuel cells (AFCs) have several advantages that overcome some of the PEMFC's scientific and technological difficulties. These advantages include: (1) the enhancement of both fuel oxidation and oxygen reduction reaction kinetics, thereby allowing the use of non-noble metal catalysts (e.g. silver, nickel and palladium), (2) the metals suffering less corrosion and are thus more stable in alkaline environments, (3) improved water management, i.e. the electroosmotic drag transports water away from the cathode, and (4) low fuel permeability, due to hydroxide ion transport, from the cathode to the anode [5–9].

The anion exchange membrane (AEM) that plays a crucial role in separating fuel and oxygen (or air) while achieving simultaneous anion transfer is one of the key components in AEMFCs. AEMs have the following requirements: adequate mechanical strength, good thermal and chemical stability and suitable ionic conductivity. To meet such demands, most studies use polymeric materials containing quaternary ammonium groups, e.g. quaternized polysulfone, [10–13] poly(2,6-dimethyl-1,4-phenylene oxide), [14] cardo polyetherketone (PEK-C), [15] poly(phenylene), [16] and radiation-grafted PVDF, ETFT and FEP, [17–19]. Unfortunately, the quaternized polymer is unstable in alkaline media at temperatures above 60 °C and at high KOH concentrations [20,21]. Moreover, there are still some outstanding problems confronting the development of AEMs for AEMFC applications, such as, the chemical stability of the cationic groups attached to the AEMs, the lower conductivity of AEMs compared with PEMs, and their overall cost-effectiveness; thus, the development of cost-effective, easily prepared, high-performance AEMs remains an unmet need.

It is well known that incorporating inorganic fillers into polymer electrolytes can alter and improve their physical and chemical properties [22–25]. In addition, the approach of using carbon nanofillers in the polymer electrolyte fuel cell's membrane has also led to a remarkable improvement in membrane performance – in terms of ionic conductivity, mechanical properties and methanol permeability [26–29]. Membranes modified with these nanosized inorganic/carbon fillers have shown encouraging results in both PEMs and AEMs.

Graphene nanosheets are considered effective polymer fillers and have been incorporated into fuel cell polymer matrices. For example, a Nafion membrane, incorporating 0.5 wt% sulfonated graphene oxide (SGO), showed an enhancement in proton conductivity of ~66% and a significantly reduced methanol permeability of ~35% [30]. In our previous study, the incorporation of 0.5 wt% GO/poly(sodium-4-styrenesulfonate) modified graphene (PSS-G) into sulfonated polyimide (SPI) led to a significant improvement in selectivity (proton conductivity/methanol permeability), ~1.5-fold greater than Nafion 117 and 7-fold greater than pristine SPI at 30 °C, while the tensile strength increased by 76% with the addition of 0.9 wt% of GO [31]. These phenomenon have also been observed in ionic liquid (IL)-based polymer electrolyte membranes with incorporated IL polymer modified graphene [PIL(NTFSI)-G] giving enhancements in ionic conductivity (257.4%) and mechanical properties (345% improvement in tensile strength and a near 25-fold increase in modulus at 150 °C) with a minimal loading of PIL(NTFSI)-G (0.5 wt%) [32]. However, the incorporation of graphene into AEMs has not been previously reported.

One key factor affecting the performance of graphene-based nanocomposite membranes is the dispersion of nanofillers in the polymer matrix. To successfully realize the reinforcing potential of graphene nanosheets, they must be fully exfoliated. GO can be easily dispersed in water; thus, hydrophilic polymers, or water-soluble polymers, are suitable polymer matrices for polymer/

graphene nanocomposites, due to their dispersion properties. Poly(vinyl alcohol) (PVA) is a hydroxyl-rich, water-soluble, biocompatible and non-toxic polymer that is commonly used in fuel cells, drug delivery, coating materials, adhesives etc. [33]. When graphene/GO is well dispersed, at the molecular level, e.g. in PVA, it significantly enhances the resulting material's mechanical properties, thermal stability and electrical conductivity [34–39].

Here, we used a simple technique to prepare graphene/PVA nanocomposite membranes by incorporating GO into a PVA matrix, using water as the processing solvent, followed by hydrazine hydrate reduction, film casting, and finishing by alkaline doping. In these PVA/graphene composite membranes, the graphene nanosheets are uniformly dispersed – resulting in continuous, well-connected tortuous ionic channels. This approach introduces sought after transport behaviour properties into the nanocomposite membranes, e.g. high ionic conductivity, low methanol permeability and low activation energy for ionic conduction. Additionally, the graphene nanosheets exhibit strong interfacial strength with the PVA matrix thereby conferring significantly enhanced mechanical properties.

2. Experimental section

2.1. Composite membrane preparation

Scheme 1 illustrates the preparation of PVA/graphene composite membranes, together with an inner structural model of PVA/graphene, at each stage after doping with KOH solution. PVA powder was dissolved in deionized (D.I.) water at 90 °C in a three-necked flask with mechanical stirring to form an aqueous solution (0.1 g mL⁻¹). GO was prepared according to the method described in our previous study and purified by centrifugation [22,31,32]. The resulting concentrated GO was diluted to 5 mg mL⁻¹. An aqueous GO suspension (5 mg mL⁻¹) was dripped into the PVA solution and stirred at 90 °C for 6 h (step a). The homogeneous dispersion was mixed with a hydrazine solution (mass ratio of hydrazine hydrate:GO = 1:1) and stirred for 1 h at 90 °C (step b). The dispersion was cast onto clean plastic plates at 60 °C for 1 day in a thermal oven to allow film formation (step c). The membrane was peeled-off the plastic plates and soaked in a reaction solution containing 10 mass % glutaraldehyde (GA) (25 wt% solution in water) in acetone at 30 °C for 1 h to give flat membranes [thickness 100–120 μm (step d)]. The thickness of the membranes was able to be well controlled by adjusting the suspension volume.

The preparation of the PVA and PVA/graphene composite membranes was conducted by immersing the membranes in various concentrations of KOH solution at 80 °C for 24 h (step e). The KOH absorbed on the surface of the membranes was removed by repeatedly rinsing in D.I. water (until pH ~7) after which they were stored in D.I. water at room temperature prior to use (step f).

2.2. Characterization of composite membranes

A DuPont Q100 thermo-gravimetric analyzer (TGA) was used to investigate the thermal stability of the membranes. Samples (~10 mg) were heated from ambient temperature to 850 °C, under a nitrogen atmosphere, at a heating rate of 20 °C min⁻¹. A tensile strength elongation test was carried out using a universal testing machine (EZ-L-500N; SHIMADZU, Kyoto, Japan). The thicknesses of the test specimens, dimensions 5 mm–50 mm, were measured using a constant crosshead speed of 5 mm min⁻¹.

Crystallization and melting behaviours were investigated by differential scanning calorimetry (DSC). The samples were heated from 30 °C to 150 °C and then maintained at this temperature for 5 min prior to cooling to –30 °C and re-heating to 250 °C. The

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