



Permeant transport properties and cell performance of potassium hydroxide doped poly(vinyl alcohol)/fumed silica nanocomposites

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ABSTRACT

Polyvinyl alcohol/fumed silica (PVA/FS) nano-composites were prepared through a solution casting method. The water diffusivity increased as FS was incorporated into the PVA matrix. The ionic conductivity of the KOH-doped PVA composites increased with the FS concentration. Meanwhile, the methanol permeability in the resulting composites decreased with FS addition due to suppressed methanol solubility and diffusivity. The PVA/KOH and PVA/FS/KOH electrolytes were employed in direct methanol alkaline fuel cells (DMAFCs). The effects of methanol and KOH concentrations, oxygen humidification, oxygen flow rate and the operating temperature on cell performance were investigated from the standpoints of kinetics and material characteristics. Oxygen humidification was necessary and a higher oxygen flow rate improved the cell performance. The open-circuit voltage and maximum power density of the PVA/(20%)FS/KOH electrolyte increased with increasing FS concentrations and operating temperatures. Among the tested methanol and KOH concentrations, the maximum power density of 15.3 mW cm⁻² was achieved for a DMAFC consisting of a PVA/(20%)FS/KOH electrolyte with 2 M methanol and 2 M KOH as the anode feed. This inexpensive electrolyte is promising for DMAFC applications.

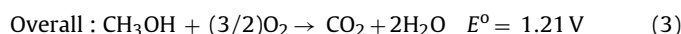
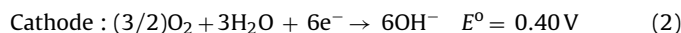
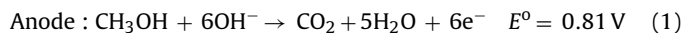
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1. Introduction

Recently, there has been increasing interest in direct methanol fuel cells (DMFCs) as alternative, portable, and power-converting sources, because methanol has a higher power density than highly compressed hydrogen and lithium-ion batteries [1,2]. In addition, DMFCs offer a number of advantages, including the use of a liquid fuel for power, a simple system design and the potential for low-volume, lightweight packaging, eliminating the need for fuel reforming and lower CO₂ emission power systems than fossil oil [3,4]. The proton-exchange membrane used in hydrogen fuel cells can be employed in DMFCs, and this process has attracted much attention. The operating principle of DMFCs using proton-exchange membranes is illustrated in Fig. 1(a). However, proton-conducting membranes, such as Nafion, suffer from methanol crossover through the electrolytes [5–8]. This leads to fuel loss, unwanted methanol oxidation potential and poisoning by CO formation on the Pt cathode catalyst [9]. In addition to decreased cell performance [10–13], the high cost of Nafion membranes and platinum-based catalysts place additional incentive on the development of alternative electrolyte and catalyst materials.

Recently, many reports on the use of direct methanol alkaline fuel cells (DMAFCs) to overcome these problems [14–18] have become available. In DMAFCs, cheaper catalysts, i.e., nickel or silver, can be used instead of more expensive Pt [19]. The methanol oxidation rate is faster in an alkaline media than in an acidic solution [20–23]. In addition, the OH⁻ anion transport direction opposes that of the methanol flux through the membrane, leading to an intrinsic reduction in methanol permeability.

In a DMAFC, the methanol and alkali solution is fed into the anode, and the reactants are converted to carbon dioxide, water, and electrons (shown in the half-reaction in Eq. (1)). Humidified oxygen reacts with electrons and produces hydroxide ions, as illustrated in the half-reaction in Eq. (2). The overall reaction is the same as the combustion of methanol (as in Eq. (3)). Fig. 1(b) demonstrates the working principle of the DMAFC.



where E^0 is the standard potential at 298.15 K and 1 bar.

Although DMAFCs can be fabricated using alkali solutions as electrolytes [24], such cells usually suffer from solution leakage, high carbon dioxide sensitivity and corrosion issues [25,26]. In the past decade, many researchers have proposed the

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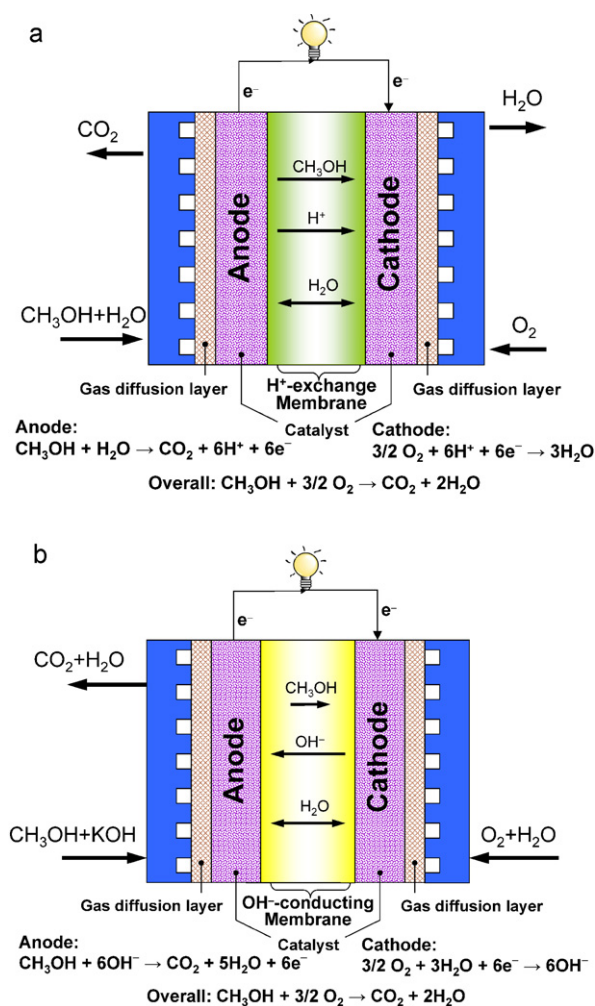


Fig. 1. Schematic showing the working principle of direct methanol fuel cells with (a) proton-exchange and (b) hydroxide-conducting membrane electrolytes.

development of DMAFCs using anion-exchange membranes that can selectively transport hydroxide ions (OH^-) [27–31]. Most of the researchers obtained maximum power densities below 10 mW cm^{-2} [15,32–35], which is not satisfactory. Alkaline-doped polymer films seem to be another class of potential electrolytes, as they are inexpensive, highly conductive and easy to fabricate. Yang et al. [17,36] synthesized KOH-doped poly(vinyl alcohol) (PVA)/ TiO_2 and PVA/sulfosuccinic acid composites as electrolytes for a DMAFC and reported that the maximum power density (P_{max}) of their DMAFC was less than 7.54 mW cm^{-2} at 60°C . They also developed a PVA/hydroxyapatite (HAP) composite [37] and quaternized PVA/(10 wt%) Al_2O_3 nanocomposite polymer membrane [38] for DMAFC. Wang et al. [39] reported that it is possible to use non-platinum Hypermectm catalyst for direct ethanol alkaline fuel cell using the poly(vinyl alcohol)/3-(trimethylammonium) propyl-functionalized silica hybrid membranes (PVA-TMAPS). Hou et al. prepared a KOH-doped polybenzimidazole (PBI) membrane electrolyte for DMAFCs and reported that the P_{max} was 31 mW cm^{-2} at 90°C when the anode was fed with a solution containing 2 M methanol and 2 M KOH [40].

Polyvinyl alcohol (PVA) is a commercially available, water-soluble polymer with good film forming characteristics, a hydrophilic nature and adhesive properties. It has been used in desalination and pervaporation membranes. In addition, it has excellent perm-selective characteristics and can selectively transport water molecules over ethanol or methanol [41–43]. In our

previous report, we showed that fumed silica (FS)-modified PVA composites exhibit higher thermal stability and lower crystallinity than the pristine polymer (Table 1 and [44]). The resulting enlarged free volume [45] may increase water transport in the PVA/FS composite and increase the ionic conductivity [46]. In addition, incorporation of micron- or nano-sized fillers into PVA resulted in lower methanol permeability, as illustrated by Yang et al. [47] and Xu et al. [48]. These characteristics are desirable for DMFC application.

The scope of the present work is to study the water and methanol uptakes and diffusivities in PVA and PVA/FS composites. The effects of oxygen humidification, oxygen flow rates, methanol and KOH concentrations (1–2 M), and FS addition on cell performance were reported. Furthermore, the methanol permeabilities of the PVA and PVA/FS and the ionic conductivities of the PVA/KOH and PVA/FS/KOH electrolytes were investigated and correlated with the cell performance. The DMAFC performance using higher KOH concentration based on these electrolytes is reported in a separate paper [49].

2. Experimental

2.1. Materials

PVA (average molecular weight of 89,000–98,000, more than 99% hydrolyzed), methanol and KOH were purchased from Sigma–Aldrich (St. Louis, MO, USA). Fumed silica (FS) with a primary particle size of 14 nm was obtained from Cabot Corp. (Carb-O-Sil M5, Tuscola, IL, USA). The materials were used as received. Pure water, of $18 \text{ M}\Omega \text{ cm}$ resistivity, was produced using a Millipore water purifier (Elix 5/Milli-Q Gradient system, Millipore Corp., Bedford, MA, USA).

2.2. Membrane and electrolyte preparation

The PVA film and PVA/FS composites were prepared using a solution casting method as described in our previous papers [44,49]. The PVA and PVA/FS membranes were immersed in 1 or 2 M KOH solution to produce PVA/KOH and PVA/FS/KOH electrolytes [49]. The characteristic properties of the PVA film and PVA/(20%)FS composite are shown in Table 1. The thickness of the resulting membrane was $180 \pm 20 \mu\text{m}$, as measured using a digital meter (Model No. 345, Elcometer Instruments Ltd., Edge Lane, England). The prepared membranes were denoted as PVA and PVA/FS. These membranes were immersed in KOH solutions (1–2 M, the same

Table 1
 Characterization of the PVA film and PVA/(20%)FS composite.^a

Property	PVA	PVA/(20%)FS
Polymer crystallinity (%), dry film ^b	51.45 ± 0.546	44.07 ± 1.161
Polymer free volume (%) ^c	1.70 ± 0.06	2.35 ± 0.06
Dissolution (%) ^{b,d}	21.39 ± 0.005	10.37 ± 1.501
Water uptake (g g^{-1}) ^e	2.714 ± 0.023	1.263 ± 0.015
Water diffusion coefficient ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$) ^e	5.944 ± 0.905	10.69 ± 1.110
Methanol uptake (g g^{-1}) ^f	0.198 ± 0.020	0.030 ± 0.007
Methanol diffusion coefficient ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$) ^f	1.777 ± 0.029	1.573 ± 0.353

^a Mean \pm standard deviation, $N=2$ except for polymer free volume data. Their errors are based on regression, as indicated in [45].

^b Source: Lue et al. [44].

^c Source: Lue et al. [45].

^d Immersed in water at 25°C for 3 days.

^e At room temperature.

^f At 60°C .

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