



Alkaline direct ethanol fuel cell performance using alkali-impregnated polyvinyl alcohol/functionalized carbon nano-tube solid electrolytes



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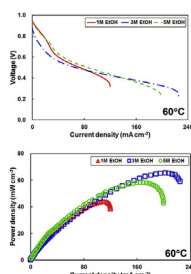
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HIGHLIGHTS

- Carbon nano-tubes are functionalized with polyvinyl alcohol.
- KOH-doped PVA/m-CNT membrane electrolyte is prepared and characterized.
- Ion conductivity of composite electrolyte is enhanced by 51.9%.
- P_{max} of ADEFC increases from 31 to 65 $mW\ cm^{-2}$ using the composite.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 August 2015

Received in revised form

8 October 2015

Accepted 28 October 2015

Available online 14 November 2015

Keywords:

Alkaline direct ethanol fuel cell (ADEFC)

Cell performance

Ethanol permeability

Conductivity

Nano-composite

ABSTRACT

This study investigates the application of a polyvinyl alcohol (PVA)/functionalized carbon nano-tubes (m-CNTs) composite in alkaline direct ethanol fuel cells (ADEFC). The m-CNTs are functionalized with PVA using the ozone mediation method, and the PVA composite containing the modified CNTs is prepared. Adding m-CNT into the PVA matrix enhances the alkaline uptake and the ionic conductivity of the KOH-doped electrolyte. Meanwhile, the m-CNT-containing membrane exhibited a lower swelling ratio and suppressed ethanol permeability compared to the pristine PVA film. The optimal condition for the ADEFC is determined to be under operation at an anode feed of 3 M ethanol in a 5 M KOH solution (at a flow rate of 5 $cm^3\ min^{-1}$) with a cathode feed of moisturized oxygen (with a flow rate of 100 $cm^3\ min^{-1}$) and the KOH-doped PVA/m-CNT electrolyte. We achieved a peak power density value of 65 $mW\ cm^{-2}$ at 60 °C, which is the highest among the ADEFC literature data and several times higher than the proton-exchange direct ethanol fuel cells using sulfonated membrane electrolytes. Therefore, the KOH-doped PVA/m-CNT electrolyte is a suitable solid electrolyte for ADEFCs and has potential for commercialization in alkaline fuel cell applications.

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1. Introduction

The growing global energy demand and large-scale use of carbon dioxide-emitting fossil fuels pose a great threat to our planet. Therefore, developing renewable energy sources at a global scale is urgent for the sustainable development of our society. Fuel cells

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have been identified as one of the most promising technologies for the clean energy industry of the future. Fuel cells convert chemical energy stored in fuel, such as hydrogen, into electrical energy output through electrochemical reactions. Currently, hydrogen is commonly used as fuel to energize fuel cells, particularly proton exchange membrane fuel cells (PEMFCs). However, the production of pure hydrogen is currently expensive and there are tremendous challenges in transporting, storing, and handling gaseous hydrogen. For this reason, liquid hydrogen-rich alcohol fuels, which have a much higher energy density and are easier to transport, store, and handle, have become an attractive alternative to hydrogen for direct oxidation fuel cells. Consequently, direct alcohol fuel cells (DAFCs) have become promising for their lightweight fluid reservoir and simple systems, especially for portable and mobile applications.

Among various alcohol fuels, direct methanol fuel cells (DMFCs) have been extensively studied over the past few decades because methanol has a simple molecular structure for easy oxidization; thus, there is the potential that it has better electrode kinetics than other alcohol fuels [1]. However, there are several challenges for direct methanol fuel cell development, including high methanol crossover [2], electrode instability [3], and methanol's high toxicity [1]. In contrast, ethanol is more environmentally friendly and possesses a higher energy density than methanol (8.00 vs. 6.09 kWh kg⁻¹ [4]). Ethanol can be easily produced in large quantities from the biological processing of agriculture products and is considered a renewable energy source [5]. Furthermore, the ethanol permeability is lower than that of methanol in many electrolyte membranes [6,7], which is beneficial for minimizing fuel crossover and catalyst poisoning [8]. Therefore, direct ethanol fuel cells (DEFCs) have received increasing attention in recent years [1,9].

DEFCs may be operated in an acidic or an alkaline mode. The challenges associated with developing an acidic DEFC include slow ethanol oxidation reaction kinetics (which cause serious activation polarization loss), the propensity of electrode catalysts to corrosion in an acidic environment (which results in poor fuel cell durability), and high costs of precious metal-based electrocatalysts and acid electrolyte membranes (typically Nafion) [1,2]. Several potential benefits may be obtained in alkaline fuel cell operations. The oxygen reduction and ethanol oxidation react faster in alkaline solution than in acidic mode, allowing the use of non-platinum catalysts. The fuel crossover is alleviated as the hydroxide ions produced at the cathode tend to be transported towards the anode, opposite the direction of the fuel diffusion paths. Water is produced at the anode and consumed at the cathode. Thus, the water management regime is potentially simplified, and the problem of cathode flooding is avoided [10]. Furthermore, inexpensive hydroxide-conducting electrolyte membranes may be used to replace pricy perfluorosulfonic acid membranes. It has been shown that when the acid electrolyte is changed to alkaline media, the DEFC efficiency increases [4]. These benefits make the alkaline direct ethanol fuel cell (ADEFC) a promising power generation system for both portable and stationary devices [2,11–13].

Efforts on advancing ADEFCs include the development of catalysts [14,15], membrane electrolytes, single cell design, and improvements in operating conditions. Several extensive review articles have been published on these aspects by Zhao et al., Antolini and Gonzalez, Yu et al., and Kamarudin et al. [2,4,16,17] along with ADEFC performance data, summarized therein [16,17]. Palladium and palladium-nickel catalysts were reported to show promising cell performance [14] but the activity stability remains a serious challenge [18–20]. Aside from catalyst development, solid polymer electrolyte membranes is another hot research topic for ADEFCs. An effective electrolyte membrane needs to exhibit

sufficient ionic conductivity, good mechanical strength, chemical and thermal stability, and suppressed fuel permeability. There are three categories of electrolyte membranes for ADEFC applications. The first one contains fixed functional moieties (such as quaternary ammonium) on the polymer backbone, similar to anion-exchange membranes, which allow selective transport of hydroxide ions (OH⁻) [21,22]. The second category of electrolyte membranes contains electronegative heteroatoms (such as oxygen or nitrogen) that interact with the alkali by a donor-acceptor link after being doped with an alkali solution. The ions migrate through the polymeric matrix, preferably through the amorphous regions or polymeric free volumes [2,23]. Potassium hydroxide (KOH)-doped polybenzimidazole (PBI) is a typical example [24] in this category. The third category is organic-inorganic composite electrolytes manufactured by incorporating a small amount of inorganic fillers into a polymeric matrix. The addition of nanocrystalline titanium oxide (TiO₂), hydroxyapatite (HAP), montmorillonite (MMT), or fumed silica (SiO₂) into polyvinyl alcohol (PVA) increases ionic conductivity, dimensional stability, and enhances alkaline direct methanol fuel cell performance [7,25–27]. Stable long-term alkaline fuel cell performance using the PVA-based composites has been reported [19,28]. Representative ADEFC performance data with some electrolyte membranes, including ion-exchange membranes and KOH-doped PBI or PVA derivatives, are summarized in Table 1 [29–31].

Incorporating carbon nano-tubes (CNTs) into membrane matrices has demonstrated promising improvements in fuel cell performance. Several researchers have reported that adding a small amount (0.05–1 wt%) of CNTs into a polymeric electrolyte improves the ionic conductivity and acidic DMFC performance when compared with the pristine polymer film [32–36]. To improve the chemical compatibility and prevent electron leakage, Lue et al. demonstrated that CNTs need to be functionalized with polymeric chains, which enhance both the cell voltage and power density [37].

In the present research, we investigate the performance of a KOH doped-PVA/modified-CNT (m-CNT) electrolyte for ADEFC applications. The polymer crystallinity, fractional free volume, ethanol permeability, alkaline uptakes, and conductivity values of the membranes are evaluated. The power performance of an alkali-doped PVA-based ADEFC is correlated with the electrolyte characteristics, which include polymer physical properties, conductivity, and transport features. The hydroxide ion transport through Grotthus, vehicular, and surface diffusion mechanisms is determined for the PVA and PVA/m-CNT composite in the ADEFCs.

2. Experimental

2.1. Materials

Multi-walled carbon nano-tubes (CNTs) with average diameters of 10–50 nm and lengths of 1–25 μm were received from the Carbon Nano-tube Co., Ltd., Incheon, Korea. The purity of the received CNTs was 93%. The CNTs were washed with dimethylsulfoxide prior to use. Polyvinyl alcohol (PVA, average molecular weight of 89000–98000 Da, more than 99% hydrolyzed) and potassium hydroxide (KOH) were obtained from Sigma–Aldrich (St. Louis, MO, USA). Ethanol (HPLC grade, 99.9%) was acquired from Seimao Chemical Material Co. Ltd., Tainan, Taiwan. Gas diffusion electrodes with 5 mg cm⁻² Pt–Ru alloy (1:1) black for the anode and 5 mg cm⁻² Pt black for the cathode were purchased from E-tek (BASF, Ludwigshafen, Germany). They were prepared using Nafion as the binder and the gas diffusion layer was a hydrophobicity-controlled microporous layer on carbon cloth. Deionized (D.I.) water, with a resistivity of 18 MΩ-cm, was produced using a Millipore water purifier (Elix 5/Milli-Q Gradient system, Millipore

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