Journal of Power Sources 311 (2016) 188–194

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

A monolayer graphene – Nafion sandwich membrane for direct methanol fuel cells

X.H. Yan [a], Ruizhe Wu [b], J.B. Xu [a], Zhengtang Luo [b], T.S. Zhao [a, *]

[a] Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China
[b] Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

HIGHLIGHTS

- A composite membrane consisting of monolayer graphene is proposed for DMFCs.
- The methanol permeability through the membrane is demonstrated to decrease by 68%.
- The membrane enables a passive DMFC to operate with highly concentrated solutions.

ARTICLE INFO

Article history:
Received 17 December 2015
Received in revised form
6 February 2016
Accepted 8 February 2016
Available online 20 February 2016

Keywords:
Fuel cells
Direct methanol fuel cells
Monolayer graphene
High energy density

ABSTRACT

Methanol crossover due to the low selectivity of proton exchange membranes is a long-standing issue in direct methanol fuel cell technology. Here we attempt to address this issue by designing a composite membrane fabricated by sandwiching a monolayer graphene between two thin Nafion membranes to take advantage of monolayer graphene's selective permeability to only protons. The methanol permeability of the present membrane is demonstrated to have a 68.6% decrease in comparison to that of the pristine Nafion membrane. The test in a passive direct methanol fuel cell (DMFC) shows that the designed membrane retains high proton conductivity while substantially suppressing methanol crossover. As a result, the present membrane enables the passive DMFC to exhibit a decent performance even at a methanol concentration as high as 10.0 M.

1. Introduction

The proton exchange membrane (PEM) is a semi-permeable membrane typically composed of ionomer, designed to conduct protons while being impermeable to other species. It is a key component in various electrochemical energy conversion and storage systems such as fuel cells, redox flow batteries and electrolyzers. The most common PEM is perfluorosulfonic acid (PFSA) membrane which is commercially known as Nafion® and is largely recognized for its excellent proton conductivity, mechanical strength, chemical stability and durability [1–5]. However, the relatively poor selectivity of Nafion membranes between proton and other ions or small molecules results in a migration issue in electrochemical energy systems. Active species can penetrate the membrane from one electrode to the other which poses issues such as hydrogen penetration in PEM fuel cells and PEM electrolyzers, alcohol crossover in direct alcohol fuel cells, as well as redox couples crossover in redox flow batteries. Among these issues, alcohol crossover is particularly undesirable, specifically for direct methanol fuel cell (DMFC), causing mixed potential and cathodic catalyst poisoning [6–10]. Nafion membrane is especially susceptible to methanol crossover. Its hydrophilic side-chains maintain water saturation in its cluster-network that allows methanol molecules to bind via hydrogen bonding causing methanol crossover to be unavoidable. To circumvent this issue and lower the methanol permeation rate, diluted methanol solutions ranging from 1.0 M – 5.0 M have typically been employed. Although it is a viable solution, this approach severely compromises the energy density of the fuel cell.

To overcome this technical bottleneck, efforts have been focused on modifying Nafion membranes with inorganic/organic species that act as physical barriers preventing methanol crossover. Numerous inorganic materials have been reported as effective

* Corresponding author.
E-mail address: metzhao@ust.hk (T.S. Zhao).

http://dx.doi.org/10.1016/j.jpowsour.2016.02.030
0378-7753/

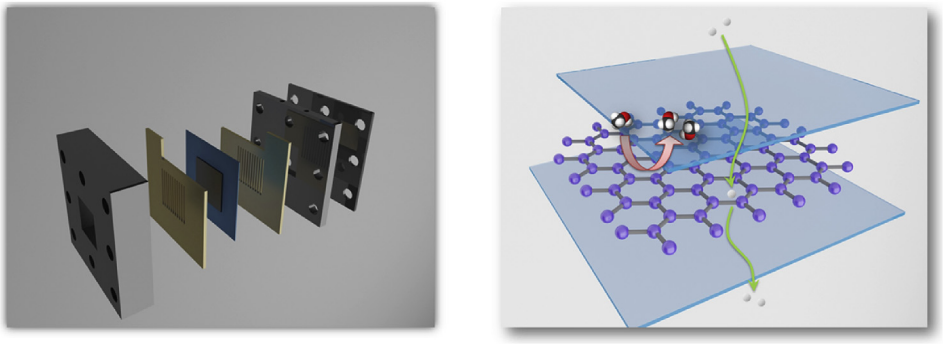

Fig. 1. Schematic illustration of a monolayer graphene film sandwich membrane based passive direct methanol fuel cell. The left side is the setup of the passive DMFC; the right side is the sandwich membrane assembling graphene film and Nafion membranes.

fillers to improve the properties of Nafion membrane such as titanium dioxide [11], silica [12], organo-modified silica [13], zirconium phosphate [14], phosphotungstic acid [15], Na-X zeolite [16], graphene oxide nanosheet [17], functionalized graphene oxide [18] and other various types of nanomaterials [19]. Blending Nafion with different polymers is also an effective approach. Polymers such as polyvinylidene fluoride [20], polybenzimidazole [21] and polyaniline [22] have been used to reduce methanol crossover. Many of these previous approaches attempt to alter the microstructure of Nafion membranes so that water uptake is reduced consequently slowing down the migration rate of active species. However, these methods undesirably sacrifice proton conductivity to varying degrees.

In the recent literature, it has been reported that a perfect graphene monolayer is impermeable to all atoms and molecules under ambient conditions but highly permeable to protons [23]. Based on this finding, we propose a composite membrane fabricated by sandwiching a monolayer graphene film between two Nafion membranes, as illustrated in Fig. 1. Unlike previous studies that alter the intrinsic property of Nafion membranes, the monolayer graphene functions as a sieve to increase membrane selectivity. We evaluated this membrane in a passive direct methanol fuel cell by demonstrating significantly suppressed methanol crossover while maintaining high proton conductivity. The high selectivity and high proton conductivity of this membrane are mainly attributed to the joint effect of the sieving nature of monolayer graphene and the existing defects at different scales.

2. Experimental

2.1. Graphene film synthesis by chemical vapor deposition and membrane fabrication

Copper foil purchased from Alfa Aesar (>99.8%, No. 13382) was used to synthesize graphene film. The copper foil was chemically polished with etchant solution consisting of 5 g $FeCl_3$ (≥99%, Sigma-Aldrich), 10 mL HCl (analytical reagent, VWR International) and 100 mL DI water, ultrasonicated for 10–15 s and rinsed with 10% HCl solution and DI water three times to remove residues. The copper foil was subsequently blow-dried with nitrogen.

The polished copper foil was loaded into a 1.0-inch diameter quartz tube and purged with 350 sccm high-purity argon gas (Hong Kong Specialty Gases Co., Ltd., 99.999%, oxygen concentration <3 ppm) and 15 sccm hydrogen gas (Hong Kong Specialty Gases Co., Ltd., 99.999%, oxygen concentration <5 ppm) for at least 20 min. The system temperature was then ramped to 1050 °C within 30 min in Ar/H_2, followed by charging with 15 sccm diluted methane (500 ppm methane diluted in argon, Arkonic Gases and Chemicals Inc., 99.99%) and kept for 30 min for the growth of the monolayer graphene film. Finally, the copper with graphene film was rapidly cooled to room temperature in an atmosphere of Ar/H_2 gas.

After chemical vapor deposition, Nafion ionomer (D520 Alcohol based 1000 EW at 5% weight, DuPont) was spin-coated on the graphene/copper surface as the supporting layer with an approximate thickness of 700 nm. Then, the Cu foil was dissolved in $FeCl_3$ based etchant to release the Nafion ionomer/graphene film. Subsequently, the Nafion ionomer/graphene was rinsed with 10% HCl

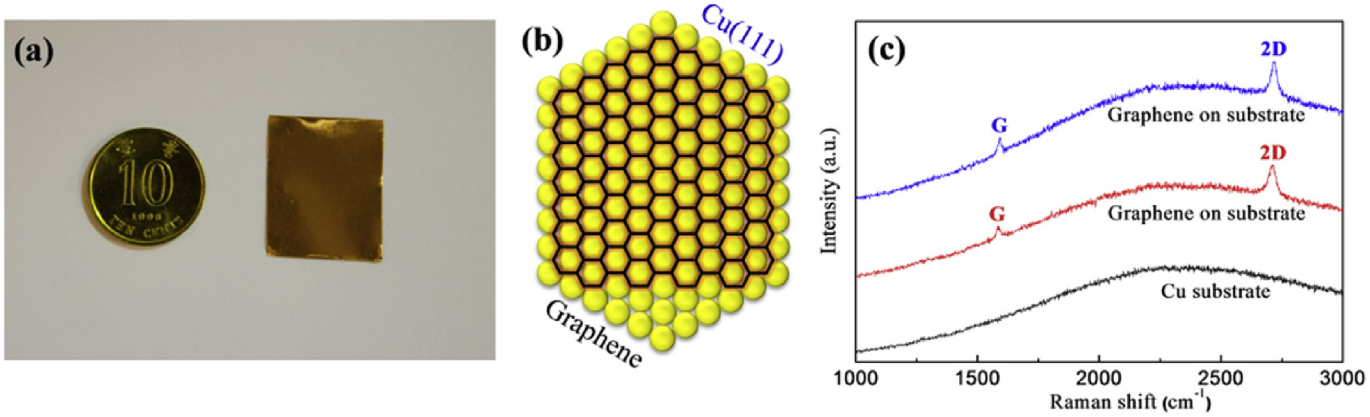

Fig. 2. (a) Photograph of the synthesized centimeter-scale CVD graphene on the copper foil substrate; (b) Illustration of atomic configuration of graphene films on Cu crystal plane; (c) Raman spectrum at 2 random sites of Graphene on Cu foil and Raman spectrum of pure Cu foil.