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High performance direct methanol fuel cells with micro/nano-patterned polymer electrolyte membrane

Yoon-Hwan Cho [a,b], Jin Woo Bae [b], Ok-Hee Kim [a,b], Jae Young Jho [b], Namgee Jung [a,b], Kyusoon Shin [b], Hyelim Choi [c], Heeman Choe [c], Yong-Hun Cho [c,*], Yung-Eun Sung [a,b,1]

[a] Centre for Nanoparticle Research, Institute for Basic Science (IBS), Seoul National University, Seoul 151-744, South Korea
[b] School of Chemical and Biological Engineering, Seoul National University (SNU), Seoul 151-744, South Korea
[c] School of Advanced Materials Engineering, Kookmin University, 861-1 Jeongneung-dong, Seoul 136-702, Seongbuk-gu, South Korea

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ABSTRACT

The effect of an enlarged specific surface area of the membrane with well-defined line patterns on the performance of a direct methanol fuel cell (DMFC) is investigated and compared with the baseline pristine Nafion 115 membrane. Line patterns with dimensions ranging from several tens of nanometers to several micrometers were fabricated on Nafion 115 membranes with high reliability using thermal imprint lithography to ensure an uncollapsible structure. In the case of quasi-nano-patterned membrane the cell performance increased about 35% compared with that of the pristine Nafion 115 membrane owing to an increased effective three-phase boundary caused by an enlarged specific surface area. Thus the performance of DMFCs can be improved further by controlling the shape and size of the line patterns for sufficient formation of the three-phase boundary.

1. Introduction

The direct methanol fuel cell (DMFC) is an eco-friendly energy conversion system, generating electricity directly through the electrochemical reaction of methanol and oxygen [1,2]. Moreover, the DMFC is one of the best alternative portable power sources owing to its high energy density as well as the ease with which it can be applied to small electronic devices [3,4]. On the other hand, resolving its cost issue, which stems primarily from the use of a Pt catalyst in the membrane–electrode assembly (MEA), remains the largest obstacle to the widespread application of DMFCs to mobile and stationary platforms [5,6]. Accordingly, many attempts have been made to reduce the amount of Pt in the catalyst layer without deteriorating the DMFC performance [7–11].

Several methods of creating as large a 'three-phase boundary' area as possible, where the reactants, catalysts and electrolyte coexist in the MEA, have attracted considerable interest because they might improve the electrochemical performance of DMFCs and reduce the amount of Pt catalyst needed. For example, roughening the surface of the electrolyte membrane comprising the three-phase boundary in the MEA has been attempted recently. Since Sheppard et al. first reported that the electrolyte membrane could be roughened by SiC paper [12,13], additional investigations into modifying the surface structure of the electrolyte membrane have been performed by plasma etching or ion beam bombardment [14–17]. Yildirim and coworkers reported the increased MEA performance with micro-patterned Nafion 117 membrane using a hot embossing process [18]. DMFC performance of electron beam patterned membrane was further investigated by Omosebi and Besser [19]. Nevertheless, previously modified electrolyte membranes with large specific surface areas had some limitations regarding the electrochemical fuel cell performance. The whisker-like structure of the surface-modified electrolyte membranes collapsed readily during MEA preparation, which disrupted the three-phase boundary where the electrochemical reaction occurred. Therefore, it is essential to design an electrolyte membrane with both an enlarged surface area and robust surface structure so that an effective three-phase boundary with the loaded catalysts and reactants can be formed in the MEA, which thus improves the conversion efficiency of electrochemical energy in DMFCs.

This communication reports the improved single-cell performance of electrolyte membranes containing well-defined micro-sized, quasi-nano-sized and nano-sized line patterns. The line patterns were introduced to the electrolyte membrane to ensure an uncollapsible structure with a high-specific surface area. Uniform line patterns, ranging in size from several tens of nanometers to several tens of

* Corresponding author. Tel.: +82 2 910 5672; fax: +82 2 910 5674.
E-mail addresses: yhun00@kookmin.ac.kr (Y.-H. Cho), ysung@snu.ac.kr (Y.-E. Sung).
[1] Tel.: +82 2 880 1889; fax: +82 2 888 1604.

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micrometers, were developed to measure quantitatively the effect of an enlarged specific membrane surface area on the performance of DMFCs. The well-defined line patterns were imprinted on both sides of an electrolyte membrane by thermal imprint lithography (TIL) [20–22]. TIL is expected to increase the reactive surface area of the three-phase boundary and enhance the performance of DMFCs considerably because a wide range of well-defined line patterns can be fabricated on an electrolyte membrane without collapsing the structure.

2. Experimental methods

2.1. Preparation of micro-patterned master molds [23]

Periodic micro-scaled and quasi-nano-scaled Si line patterns were fabricated using photolithography at the Korea Advanced Nano Fab Center (KANC). An n-type Si (100) wafer (MEMC Electronic Materials, Inc.) was etched by piranha solution (3:1 mixture of concentrated sulfuric acid and 30% hydrogen peroxide) at room temperature for 1 h and ultrasonicated with acetone to clean the surface of Si wafer. Photoresist (AZ7210) was spun-cast on the cleaned Si wafer substrate at 3000 rpm resulting in 1 μm thick layer, followed by baking at 100 °C for 90 s. Exposure was performed with a manual mask aligner (EVD620, EVD) at 40 mJ cm^{-2} and followed by post-exposure bake at 110 °C for 60 s. After development, the patterned photoresist on the Si wafer was baked at 120 °C for 90 s and the Si wafer substrate was selectively etched with inductively coupled plasma (Multiplex ICP, STS). Leftover photoresist on the etched Si wafer was removed with the Microwave Asher (ALA-0601E, AMS). Height and line intervals of the two patterns are 1 μm and 15 μm, and 700 nm and 700 nm for micro-scaled and quasi-nano-scaled patterns, respectively.

2.2. Preparation of nano-patterned master mold [24]

Periodic nano-scaled Si line pattern was fabricated using e-beam lithography (JBX9300FS, JEOL) at the Korea Advanced Nano Fab Center (KANC). Height and line intervals of the periodic nano-scaled Si master mold were 70 nm and 200 nm, respectively, upon which several Rigiflex master molds were replicated. ZEP 520A was used as an e-beam resist and the exposure does used was 300 μC cm^{-2}. UV-curable polymer solution (MINS 311, Minuta tech.) was dropped on the Si master line pattern template. Adhesion promoter-coated PET film (Minuta tech.) was then placed on top of the MINS 311 as a supporting layer. After UV-curing for 20 s, rigiflex master mold was physically detached from the Si master. Prior to use, the rigiflex master molds were aged for several hours.

2.3. Fabrication of MEAs with the patterned Nafion membranes and the pristine Nafion 115 membrane

Fabrication of the MEA with the line-patterned Nafion membrane is shown schematically in Fig. 1. Nafion 115 membrane (equivalent weight value = 1100 g $eq.^{-1}$, thickness: 120 μm, DuPont) was used as a polymer electrolyte membrane for the DMFC. First, line-patterned master molds were in contact with both sides of Nafion 115 membrane, and pressed with 200 Pa at 180 °C for 1 h in a vacuum oven. Following slow cooling to room temperature and release of mechanical pressure, the resulting Nafion membranes were immersed in distilled water for 24 h at 50 °C so that the patterned Nafion membrane can naturally detach from the master molds. To remove remaining impurities prior to applying the patterned Nafion membrane to the MEA, the patterned Nafion membranes were treated sequentially in a 3 wt% solution of hydrogen peroxide, distilled water, 0.5 M sulfuric acid, and distilled water, each at 70 °C

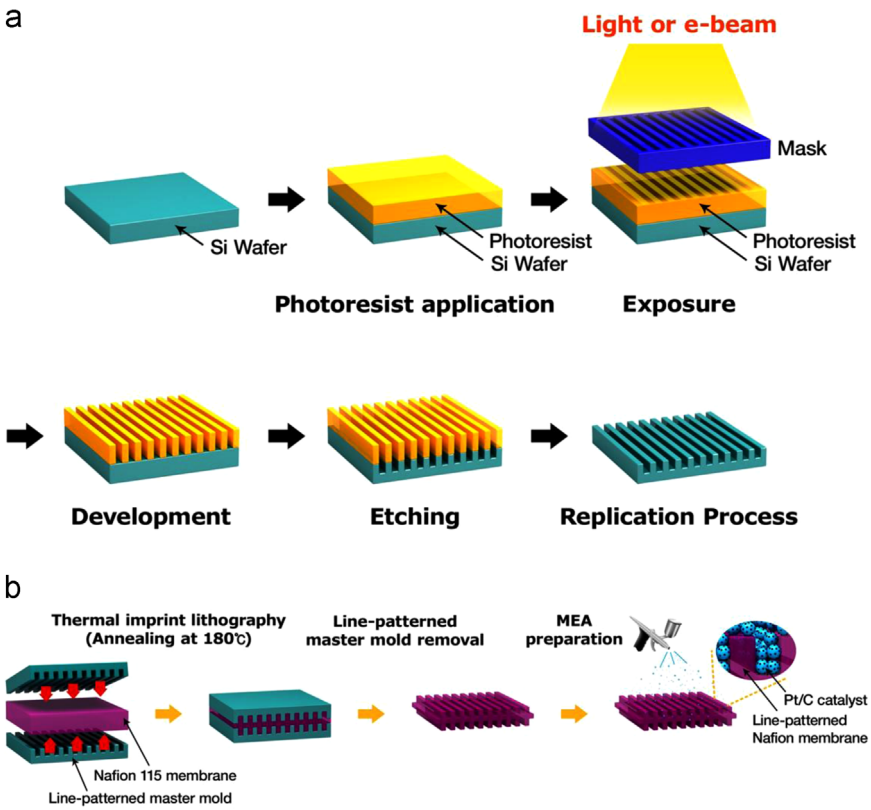

Fig. 1. Schematic illustration of the fabrication of the MEA using the line-patterned Nafion membrane. (a) Line patterns on both sides of the Nafion 115 membrane were replicated by the master molds using TIL. And then, (b) the MEA was fabricated by directly spraying the Pt/C catalyst ink onto the both sides of line-patterned Nafion membrane without a hot-pressing process.