



## Microstructure-modified proton exchange membranes for high-performance direct methanol fuel cells



Manxiang Wang<sup>a,b,1</sup>, Guicheng Liu<sup>b,\*,1</sup>, Zhe Tian<sup>c,1</sup>, Yingna Shao<sup>c</sup>, Lei Wang<sup>d,\*</sup>, Feng Ye<sup>e</sup>, Minh Xuan Tran<sup>b,f</sup>, Yanbin Yun<sup>a,\*</sup>, Joong Kee Lee<sup>b,f,\*</sup>

<sup>a</sup> College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China

<sup>b</sup> Center for Energy Convergence Research, Green City Research Institute, Korea Institute of Science and Technology (KIST), Hwarang-ro 14-gil 5, Seongbuk-gu, Seoul 02792, Republic of Korea

<sup>c</sup> Suzhou Smart Sustainable Energy Technologies, LLC., 68 Southeast Ave., Science and Technology Park, Suzhou Changshu, Jiangsu Province 215558, China

<sup>d</sup> Beijing Key Lab of Cryobiomedical Engineering and Key Lab of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

<sup>e</sup> Key Laboratory of Condition Monitoring and Control for Power Plant Equipment of MOE, School of Energy Power and Mechanical Engineering, North China Electric Power University, Beijing 102206, China

<sup>f</sup> Energy and Environmental Engineering, Korea University of Science and Technology, Daejeon 34113, Republic of Korea

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### ABSTRACT

To lower methanol crossover and volume swelling degree, and to improve proton conductivity, a simple hot-mould-modifying method has been introduced to modify Nafion membrane for the direct methanol fuel cell application. To evaluate effect of the modification on properties of the Nafion membrane and fuel cell performance, a series of measurements of membranes and fuel cells have been carried out. The results show that, compared with the normal membrane, the modified Nafion membrane with regular spindle-type groove array possesses higher proton conductivity and methanol diffusion resistance, and 31.9% better dimensional stability, owing to its larger electrical double-layer capacitance come from the higher contact area between electron-electrode and ion electrolyte, and its more compact internal structure. And also, the direct methanol fuel cell based on the modified Nafion membrane shows 13.3% higher discharge power density and better long-time running performance than the normal one. Furthermore, this hot-mould-modifying method could be introduced into doping/coating-modified membranes reported in the current literature to further modify Nafion membranes, because this method is compatible with the current modifications.

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### 1. Introduction

The proton exchange membrane fuel cell is considered to be a promising distributed energy generation technology [1]. Direct Methanol Fuel Cells (DMFCs) have attracted more and more attention as potential power sources for portable electronic devices in the new energy field, because of low cost of methanol, simple running operation and quick start-up [2]. To spur commercialization and development of DMFCs, we need to overcome their high fabricating cost and low discharging performance [3]. For improvement of the fuel cell performance, lots of efforts have been done [4].

Suleiman et al. [5] carried out a thermos-economic analysis for DMFCs, and determined the optimal operating parameters at 50 kW output for each step. Liu et al. [6] first introduced a gradient activation process and supplemented the activation theory. They also discussed the effect mechanism of pore-forming agent on the anodic and cathodic properties [7]. Zainoodin et al. [8] pointed that the components in the Membrane Electrode Assembly (MEA) strongly affect the fuel cell performance, and optimized a kind of porous carbon nanofiber layer for DMFCs. Thiam et al. [9] introduced the palladium-silica nanofibres as an additive to a Nafion recast membrane to lower methanol permeability, leading to a better performance than the normal Nafion membrane in DMFC applications. In short, currently, there are 3 main ways to enhance the discharging performance: running operation management, design and optimization for the diffusion and catalyst layers with novel microstructure and high electrochemical active surface area, and development of the new proton exchange membrane [10]. Among

\* Corresponding authors at: Center for Energy Convergence Research, Green City Research Institute, Korea Institute of Science and Technology (KIST), Hwarang-ro 14-gil 5, Seongbuk-gu, Seoul 02792, Republic of Korea (J.K. Lee).

E-mail addresses: [log67@163.com](mailto:log67@163.com) (G. Liu), [silu861004@163.com](mailto:silu861004@163.com) (L. Wang), [yunyanbin@bjfu.edu.cn](mailto:yunyanbin@bjfu.edu.cn) (Y. Yun), [leejk@kist.re.kr](mailto:leejk@kist.re.kr) (J.K. Lee).

<sup>1</sup> These authors contributed equally to this work.

these, the modification for the Nafion-based membrane to realize low methanol permeation and high proton conductivity is an important field.

To lower methanol permeation, coating the materials with good methanol-rejecting ability on surface of Nafion membrane is the main method for DMFCs. By doping  $\text{SiO}_2$  nanoparticles and bentonite material, Wang et al. [11] synthesized a Nafion/ $\text{SiO}_2$ /m-BOT composite membrane for DMFC application. The composite membrane shows 20.4% lower methanol crossover phenomenon, 13.88% higher discharge power density, and 32.69% lower proton conductivity than those of the commercial Nafion membrane. Kumar et al. [12] successfully sulfonated the PVdF material with help of chlorosulfonic acid, and then coated it with commercial Nafion membrane. Using the modified membrane, in Nafion-SPL case, they lower methanol crossover to 2.7% of that of normal one, and got more than 1.19 times higher performance than the normal Nafion membrane-based DMFC. Meanwhile, they also decreased the proton conductivity to 16.9% of the normal Nafion membrane. Xue et al. [13] fabricated a chitosan/polyvinyl sulfuric acid-Nafion composite membrane by a layer-by-layer self-assembly process, and obtained higher characteristic factor (ratio of proton conductivity to methanol permeability) and lower methanol permeability than those of the commercial Nafion membrane. However, they also show an expense of proton conductivity.

To improve proton conductivity of proton exchange membranes, the classical method is doping polar materials (for example, cations and countervailing anions) into the Nafion membrane to increase water holding property [14]. Kwon et al. [15] reported a sulfonated graphene-Nafion composite membrane presents better proton conductivity owing to the existence of sulfonated graphene. Moreover, via similar working mechanism, lots of other inorganic materials such as  $\text{TiO}_2$  [16],  $\text{SiO}_2$  [17], and so on, have been introduced into the Nafion membrane to enhance the proton conductivity. Besides, high working temperature, as a normal way, for example, annealing at  $130^\circ\text{C}$  which is near the glass transition temperature of the recast Nafion, could result in the membrane possessing the highest proton conductivity [18].

Obviously, it's uneasy to enhance both proton conductivity and methanol diffusion resistance at the same time. Cai et al. [19] doped a bi-functional polyamide macromolecular proton conductor into Nafion membranes, and obtained the above 60% better performance of the DMFC based on the obtained composite membrane than that of a recasted Nafion membrane, because of its 50% higher proton conductivity and 45% lower methanol permeability. Among these, the synthesis process and fabrication of composite membranes are complex. Therefore, until now, few membranes prepared by a simple operation could simultaneously satisfy low methanol crossover, high proton conductivity and good shape stability.

Herein, a simple hot-mould-modifying method has been introduced to modify Nafion membranes to realize compacted internal structure, larger surface area and stable dimensions, resulting in

high proton conductivity, low methanol permeability and low swelling degree. Therefore, by this novel membrane, the DMFC power density has been enhanced to 1.13 times of the normal Nafion membrane based fuel cell, and long-time running performance has also been improved obviously. Moreover, we can imagine that this simple method can be applied to the current modified Nafion membranes reported in the aforementioned literature, as a further modification method for DMFCs.

## 2. Experimental section

### 2.1. Modification of proton exchange membrane

Du Pont™ Nafion® 212 membrane, called normal Nafion (n-Nafion) membrane in this article, was immersed in distilled water for 1 h, and then dried in a vacuum oven at  $30^\circ\text{C}$  for 24 h. The modification for the membrane was performed as shown in Fig. 1, sandwiching the pretreated membrane between a stainless steel sheet and a metal mesh mould (shown in Fig. S1) under 3 MPa and  $135^\circ\text{C}$  for 6 min in a hot-press device (in Fig. S2). After cooling down with the same pressure, the hot-mould-modified (h-Nafion) membrane was obtained by separating the resulting membrane and the mould.

### 2.2. Assembly of fuel cells

Nafion membranes were boiled in 5 wt.%  $\text{H}_2\text{O}_2$  solution, distilled water,  $0.5\text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  solution and then distilled water, step by step, at  $80^\circ\text{C}$  for 1 h each step. Commercial carbon paper coated by micro-porous layer (H2315T10AC1 NOL, Japan) and the pretreated membrane were served as diffusion layer and electrolyte. A hot-spraying method was used to prepare catalyst layers, according to our previous works [20] by a sono-tek MEA ultrasonic spray system. MEAs with effective area of  $5\text{ cm}^2$  were obtained by transferring the catalyst layers from Teflon decal blanks to the Nafion membrane via a decal method under 7.5 MPa at  $135^\circ\text{C}$  for 3.5 min. Fuel cell was assembled by sandwiching the MEA between two diffusion layers to carry out activation processes and discharge test [21].

### 2.3. Measurements for the membranes

Surface and section morphologies of the MEA in this experiment were surveyed by a Cambridge S-360 Scanning Electron Microscope (SEM).

Water absorption of membranes, a quality ratio between the absorbed water in the membrane and the dry membrane, was tested as follow: firstly, a membrane was immersed into deionized water for 8 h. Then filter papers were used to remove the redundant surface water. And the membrane quality was measured ( $W_1$ ); subsequently, after 24 h of drying at  $80^\circ\text{C}$ , the quality of

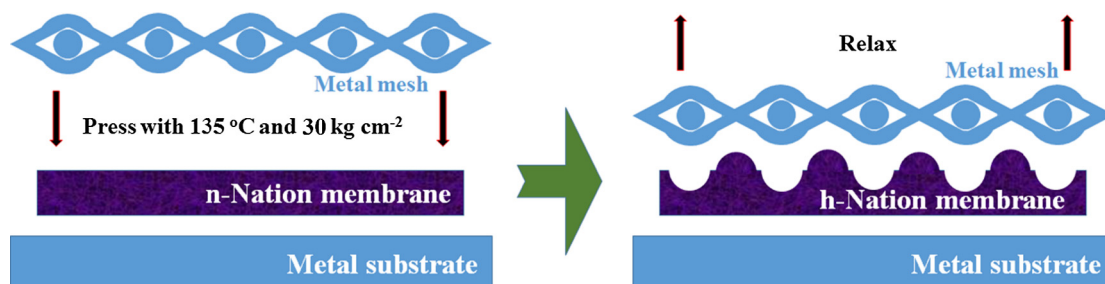


Fig. 1. Preparation sketch of the hot-mould-modified Nafion membrane (h-Nafion).

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