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Published in:
Electrochimica Acta

Link to article, DOI:
[10.1016/j.electacta.2018.01.015](https://doi.org/10.1016/j.electacta.2018.01.015)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Chen, M., Wang, M., Ding, X., Li, Q., & Wang, X. (2018). A novel catalyst layer structure based surface-patterned Nafion® membrane for high-performance direct methanol fuel cell. *Electrochimica Acta*, 263, 201-208. <https://doi.org/10.1016/j.electacta.2018.01.015>

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Accepted Manuscript

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PII: S0013-4686(18)30029-X

DOI: [10.1016/j.electacta.2018.01.015](https://doi.org/10.1016/j.electacta.2018.01.015)

Reference: EA 30997

To appear in: *Electrochimica Acta*

Received Date: 17 September 2017

Revised Date: 23 November 2017

Accepted Date: 3 January 2018

Please cite this article as: M. Chen, M. Wang, Z. Yang, X. Ding, Q. Li, X. Wang, A novel catalyst layer structure based surface-patterned Nafion[®] membrane for high-performance direct methanol fuel cell, *Electrochimica Acta* (2018), doi: 10.1016/j.electacta.2018.01.015.

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A novel catalyst layer structure based surface-patterned Nafion[®] membrane for high-performance direct methanol fuel cell

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Abstract

Conventional catalyst layer with a smooth surface exists the larger area of “catalytic dead zone” and reduces the utilization of catalyst. Based on this, a novel catalyst layer structure based surface-patterned Nafion[®] membrane was designed to achieve more efficient electrochemical reaction in this work. Surface-patterned Nafion[®] membranes were prepared by hot pressing with different pressures, and their swelling degrees reduced obviously with the increase of pressure, but proton conductivities of the membranes were almost unchanged. Pre-swelling and direct-spraying deposition methods were used to prepare the novel catalyst layer, and the effect of pressure on the performance of MEA was investigated. The results suggested that the peak power density of DMFC with optimal novel catalyst layer structure increased by 28.84%, the charge transfer resistances of anode and cathode reduced by 28.8% and 26.5% respectively, compared with the conventional catalyst layer. Performance improvement is attributed to the fact that the novel catalyst layer structure optimizes the electrolyte membrane/catalyst layer and gas diffusion layer/catalyst layer interfacial structure, which increases the electrochemical reaction region and reaction sites. The novel catalyst layer with a three-dimensional curved surface structure enlarges the “three-phase boundaries (TPB)” and electrochemical

active surface area (ECSA) of membrane electrode assembly (MEA). Therefore, this work provides an effective solution to achieve the high performance of DMFC by optimizing the internal interface structure of electrode, which is helpful to the future development of DMFC.

1. Introduction

Nowadays direct methanol fuel cells (DMFCs) are receiving more and more attention as the ideal power source for portable electronic devices, because of their large energy density, easy fuel storage, simple and compact design, green environmental protection, better security and reliability[1-4]. However, there are still many key problems to be resolved for further commercial application of DMFCs, mainly including the lower power density and electrical efficiency caused by methanol crossover[5, 6], sluggish kinetics of the anode methanol oxidation reaction (MOR)[7, 8] and cathode oxygen [9, 10] reduction reaction(ORR). The effective way to solve these problems is to improve the utilization of catalyst and increase the efficiency of electrochemical reaction[11-13]. Catalyst layer acts as the place for electrochemical reactions, and thus, plays a critical role in stable and efficient DMFC operations.

Base on this, a lot of work has been done and focused on the optimization of catalyst layer structure. For example, optimizing the ionomer (Nafion, PTFE) content to change the hydrophilicity of catalyst layer[14-16], adding pore-former to improve the porosity for better mass transfer[17, 18], and construction of gradient catalyst layer structure[19, 20]. These efforts mainly optimized the internal structure of catalyst layer, however, the electrolyte/ catalyst layer and gas diffusion layer/catalyst layer interfacial structure both remained substantially unchanged, which means that “catalytic dead zone” in the catalyst layer as described in Fig.1(a) has not been effectively reduced. As shown in Fig.1, the internal structure of DMFC is composed of flow field plate, diffusion layer, catalyst layer and electrolyte membrane. Flow field plate provides the transfer channel of reactants, then the reactants pass through the diffusion layer and enter the catalyst layer for electrochemical reaction. During this process, the reactants transfer path entering the catalyst layer is blocked in the contact

areas between diffusion layer and ribs of flow field plate, where the electrochemical reaction occurs slowly or not, namely “catalytic dead zone”. Moreover, as shown in Fig.1(a), the conventional catalyst layer has a smooth electrolyte/catalyst layer interfacial structure, and the electrochemical reaction zone is relatively small, where the “catalytic dead zone” further expands and the catalyst utilization decreases. Therefore, it is necessary to optimize the electrolyte/catalyst layer interfacial structure and reduce the adverse effects of ribs on the catalyst layer.

To optimize the interfacial structure, several groups [21-27] have reported the rough and patterned surface of Nafion[®] membrane can enlarge interfacial area between the electrolyte membrane and catalyst layer, and the performance of single cell was improved. However, these efforts ignored the effect of Nafion[®] membrane surface structure on the catalyst layer structure, and “catalytic dead zone”. For this reason, a novel catalyst layer structure based surface-patterned Nafion[®] membrane was designed as shown in Fig.2(b). It can be seen that the novel catalyst layer has a three-dimensional curved surface structure, which can effectively reduce the contact areas between diffusion layer and ribs of flow field plate. Compared with the smooth interfacial structure, the electrolyte/ catalyst layer contact interface increases obviously.

Therefore, the novel catalyst layer structure can effectively reduce “catalytic dead zone”

and enlarge electrode reaction interface to achieve the high performance of DMFC.

In this work, the above-mentioned novel catalyst layer based surface-patterned Nafion[®] membrane was designed and prepared. Firstly, stainless steel mesh was selected as the template for hot pressing to prepare surface-patterned Nafion[®] membranes. The well-defined surface-patterned Nafion[®] membrane was used to fabricate novel catalyst layer with three-dimensional curved surface structure, then fabricated membrane electrode assembly (MEA), and it was tested in DMFC single cell. The electrochemical characteristics of the DMFC single cells were measured and compared to investigate the effect of novel catalyst layer structure on the performance of DMFC.

2. Experimental

2.1 Preparation of surface-patterned Nafion[®] membranes

The Nafion[®] 115 membrane was sandwiched between two stainless steel meshes and pressed for 300 s at 150 °C under the given pressure. In order to obtain steady structure, the membrane was cooled down to 90 °C under the same pressure and kept 900 s. After cooling to room temperature, the sample was immersed in high purity water to realize the natural detachment of membrane and stainless steel mesh. Finally, the obtained surface-patterned Nafion[®] membranes were treated sequentially in 5 wt.% H₂O₂ solution, distilled water, 0.5 M H₂SO₄ solution and then distilled water, each at 80 °C for 1 h.

2.2 Membrane electrode assembly (MEA) fabrication

The MEAs were prepared by the pre-swelling and direct-spraying deposition methods[28] as shown in Fig.2. Ethylene glycol was selected as pre-swelling reagent and the surface-patterned Nafion[®] membranes were placed in ethylene glycol until fully saturated. The main reason is that ethylene glycol has higher boiling point which can ensure that the membrane does not deform during the spraying process.

Catalyst slurry was prepared as following procedures in our previous work[29-31], including catalysts, Nafion ionomer solution and isopropyl alcohol. The catalysts of anode and cathode were PtRu Black (HiSPEC 6000, Johnson Matthey) and Pt Black (HiSPEC 1000, Johnson Matthey), and the corresponding loadings were 4.0 and 3.0 mg cm⁻², respectively. Isopropanol acted as the dispersant and Nafion adhesive (5 wt. % DuPont, US) was used as proton conductor, accounted for 15 wt % and 10 wt % at anode and cathode respectively. The mixed slurry was treated by ultrasonic for 2 h, then directly sprayed on the pre-swelling Nafion[®] 115 membrane. After completing spraying, the MEA was kept in a vacuum oven for about 8 h at 65 °C to remove residual ethylene glycol from the membrane. Carbon cloth (H2315T10AC1 NOK, Japan) was served as anode and cathode diffusion layer to obtain the MEA with an active area of 5 cm² in this work.

2.3. Performance evaluation and test of DMFCs

The as-prepared MEAs were inserted into two graphite flow field plates with

serpentine channels to assemble single cell. After a series of activation operations, the DMFC performance was in-situ evaluated and monitored by 3-electrode system on self-made fuel cell test platform[32, 33]. The polarization curves were measured by potential step method at a cell temperature of 80 °C. Meanwhile, polarization curves of anode and cathode can be independently recorded by using Hg/Hg₂SO₄ reference electrode. The anode side was fed with 1.5M methanol solution at a flow rate of 5 mL min⁻¹, and the cathode side was fed with oxygen at a flow rate of 800 mL min⁻¹, and the backpressure was 0.3Mpa.

The real methanol crossover was investigated by testing the methanol limiting current of the cathode. The cathode served as work electrode and was fed with 0.3Mpa nitrogen, and anode was fed with 1.5M methanol solution as reference electrode and counter electrode. The methanol crossover was measured by linear polarization method between 0 V and 1.2 V at the scan rate of 2 mV s⁻¹ at 80 °C.

The cyclic voltammetry curves of cathode (0.05-1.35V) and anode (0.05-0.9V) were both measured to calculate the electrochemical active surface area (ECSA) at a scan rate of 50 mV s⁻¹. The measured electrode side was fed with ultra-pure water and severed as work electrode, the other electrode side was fed with hydrogen with a flow rate of 100 mL min⁻¹ and used as reference electrode and counter electrode.

Electrochemical impedance spectroscopy (EIS) of DMFCs at 400mA cm⁻² were performed using VMP2 electrochemical workstation with the frequency ranging from 99 kHz to 9 mHz.

2.4 Characterization of Nafion[®] membranes and catalyst layers

Surface morphologies of surface-patterned Nafion[®] membranes and catalyst layers in this work were observed by scanning electron microscope (FESEM, JSM-7100F). The proton conductivity of the membrane was measured by three-electrode system using Electrochemical impedance spectroscopy (EIS) method. Swelling degree of the membranes in high purity water was measured by calculating the weight change of membrane before and after water uptake.

3. Results and discussion

3.1. Characteristics of the surface-patterned Nafion[®] membranes

Stainless steel mesh was selected as the template for hot pressing to prepare surface-patterned Nafion[®] membranes, and the surface and cross-section SEM images of surface-patterned Nafion[®] membranes under different pressure conditions are shown in Fig.3. The results show that the surface of the Nafion[®] membranes becomes markedly rougher after hot pressing compared to its original smooth surface (Fig.3(a)), and the improvement of surface roughness is mainly due to the formed dent during the hot pressing. As shown in the illustrations of Fig.3(b)-(f), the depths of dents are respectively 29.7 μm , 34.9 μm , 38.8 μm , 41.2 μm , 43.1 μm , corresponding to the pressure of 0.5Mpa, 1.0Mpa, 1.5Mpa, 2.0Mpa, 2.5Mpa. The depth of dent is used to evaluate the surface roughness of membrane, so it can be seen that rougher surface could be obtained when increasing the pressure of hot pressing. Therefore, during the process of preparing MEA by direct-spraying method, the rugged surface could realize the catalyst particles distribution along the curved surface, which enlarges the contact interface between the membrane and catalyst layer, and a novel catalyst layer with three-dimensional curved surface structure can be fabricated.

In addition, swelling degree and proton conductivity of Nafion[®] membrane have a significant impact on the DMFC performance. For this reason, the effects of hot pressing on the characteristics of Nafion[®] membrane were further investigated, and the results are shown in Fig. 4. With increasing the pressure from 0.5Mpa to 2.5Mpa, swelling degrees of surface-patterned Nafion[®] membranes are respectively 17.9%, 15.9%, 14.8%, 14.2%, 14.1%, and lower than that of original Nafion[®] membrane (22.1%). It is obvious that swelling degree of Nafion[®] membrane is effectively suppressed after hot pressing, which demonstrates that hot pressing reduces the amount of freezable water in the membrane and makes the membrane structure more compact[24]. Moreover, lower swelling degree helps to reduce methanol crossover and enhance the structural stability of catalytic layer. The reduction of water content in the membrane may affect its proton conductivity, so proton conductivities of different surface-patterned Nafion[®] membranes were measured. As seen from Fig. 4, proton conductivities of original and surface-patterned Nafion[®] membranes are all around 0.1 S cm⁻¹, which show that hot pressing has little effects on the proton

conductivity of membrane. Therefore, after hot pressing, surface-patterned Nafion[®] membranes show better characteristics for DMFC.

3.2. Effects of catalyst layer structure on DMFC performance

To investigate the effects of catalyst layer structure on DMFC performance, the original and surface-patterned Nafion[®] membranes were selected to prepare MEAs, which were named MEA-HP-0Mpa, MEA-HP-0.5Mpa, MEA-HP-1.5Mpa, MEA-HP-2.5Mpa, respectively corresponding to the pressure of hot pressing. Then these MEAs were tested in DMFC single cells at 80 °C. Fig.5 shows the polarization curves and power density curves of DMFCs corresponding different MEAs. For DMFCs with surface-patterned Nafion[®] membranes, as the pressure increases, the peak power densities are 215.20 mW cm⁻², 252.72 mW cm⁻², 172.46 mW cm⁻², respectively. MEA-HP-1.5Mpa exhibits the best performance, and the peak power density is increased by 28.84% than that of MEA-HP-0Mpa (200.83mW cm⁻²). The results indicate that DMFC performance can be improved by increasing the surface roughness of Nafion[®] membrane, but too much rough surface can lead to a decrease in performance probably because of utilization loss of catalyst particles buried in the deep dents. On the other hand, as described in the polarization curves, the low current region is the electrochemical reaction control region, and the high current region is controlled by material transfer. The single cell employing MEA-HP-1.5Mpa exhibits higher cell voltage than MEA-HP-0Mpa in the above-mentioned region, indicating the novel catalyst layer structure improves the electrochemical reaction rate and optimize material transport channel.

To further understand the effects of catalyst layer structure on electrocatalysis reaction, the anode and cathode polarization curves of DMFCs were measured by 3-electrode system and shown in Fig.6(a). Apparently, the MEA-HP-2.5Mpa shows the worst performance, which may be attributed to the deeper dent causes a crack in the catalytic layer. Moreover, the MEA-HP-1.5Mpa exhibits the lowest anode and cathode polarization, and the overpotential for anode and cathode at 400mA cm⁻² reduces 22 mV and 32 mV compared with MEA-HP-0Mpa, which indicates cathode

electrocatalysis reaction rate increases more obviously. The decrease in overpotential may be mainly attributed to the increase of “three-phase boundaries (TPB)” among MEA. Especially, the enhancement of cathode electrocatalysis efficiency is likely to benefit from the reduction of methanol crossover. Because methanol crossover through Nafion[®] membrane induces mixed potential at the cathode and severely affects the performance of DMFC, methanol crossover current densities at cathode were measured and shown in Fig.6(b). It is observed that MEA-HP-0Mpa suffered the most serious methanol crossover, and the corresponding current density reaches $343.10 \text{ mA cm}^{-2}$. After hot pressing, methanol crossover current densities of the MEA-HP-0.5Mpa, MEA-HP-1.5Mpa, MEA-HP-2.5Mpa were $246.80 \text{ mA cm}^{-2}$, $213.56 \text{ mA cm}^{-2}$, $200.91 \text{ mA cm}^{-2}$, respectively. These results suggest that methanol crossover decreases with the increase of pressure for hot pressing, which are consistent with the fore-mentioned swelling degree change of membrane. It may be concluded that the lower swelling degree of surface-patterned Nafion[®] membrane improves resistance to methanol crossover, and rough surface enlarges the effective reaction region of catalyst layer and “three-phase boundaries (TPB)” in MEA.

The impedance measurements of DMFCs were performed at 400 mA cm^{-2} and applied to reveal the effect mechanism of new electrode structure. Fig. 6(c) presents the EIS measurements and equivalent circuit is described as $L_1R_m(Q_1R_c)(Q_2R_a(R_4L_2))$ [27, 32, 34]. L_1 indicates the high-frequency inductance, R_m represents the ohmic resistance mainly determined by membrane resistance, R_c and R_a denotes the charge transfer resistance of oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR), Q_1 and Q_2 are constant phase angle elements which describes the realistic reaction conditions with porous electrode and rough interface structures of cathode and anode, respectively. L_2 suggests the current is phase delayed with regard to voltage perturbation as a result of slower CO desorption, and R_4 modifies the phase delay.

The fitting results according to the equivalent circuit model are presented in Table 1, and the variations of R_m , R_c , R_a are recorded and shown in Fig. 6(d). R_m indicates the ohmic resistance mainly determined by Nafion[®] membrane resistance, and R_m of all

MEAs are around $0.16 \Omega \text{ cm}^2$, which is further proved that the proton conductivity of the membrane is not affected by hot pressing. In addition, it can be seen that the charge transfer resistances of ORR and MOR for MEA-HP-1.5Mpa are respectively $0.173 \Omega \text{ cm}^2$ and $0.158 \Omega \text{ cm}^2$, which are markedly reduced by 28.8% and 26.5% than that of MEA-HP-0Mpa. The results show that the novel catalyst layer shows higher catalytic efficiency at the same noble metal loading. Moreover, L_2 is the inductance caused by CO_{ads} on the catalyst surfaces during the methanol electrooxidation, and the smaller the value, the higher the efficiency of anode methanol oxidation reaction[35]. MEA-HP-1.5Mpa has the minimum value and exists the best performance, which corresponds to its lowest anode charge transfer resistance. On the other hand, the roughness of the catalytic layer and the interface-related kinetics are characterized by constant-phase elements rather than ideal capacitors, n_1 and n_2 are the adjustment parameters to reflect characteristics of the electrode structure. As reported in the literature[34, 36], adjustment parameter equals 1.0, which suggests that the active surface reaction sites are uniformly distributed and a relatively small fraction of catalyst participates in the electrocatalytic reaction. As seen from the Table 1, the value of n_1 is around 0.7, and that of n_2 is closer to 1.0, which indicates the surface of cathode catalyst layer is rougher than that of the anode. With the increase of pressure, the value n_1 and n_2 both reduced, but n_1 changed more obviously. For the MEA-HP-1.5Mpa, the value of n_1 decreases to around 0.665, indicating that the distribution of catalytic active sites is non-uniform, and electrochemical reaction zone extends to the inner layer of the catalytic layer. Therefore, the effective reaction region in the catalyst layer increases, and the utilization of catalyst is improved. Consequently, the novel catalyst layer can optimize the electrolyte/ catalyst layer and diffusion layer/catalyst layer interfacial structure, and increase catalyst utilization, which could be responsible for the improved performance.

However, it can be seen that MEA-HP-2.5Mpa shows the worst performance. To identify the effect of pressure on the performance of MEA, surface and cross-section SEM images of the anode and cathode catalyst layer corresponding to different MEAs were observed as shown in Fig.7. As shown in Fig.7(a), the conventional anode and

cathode catalyst layer both have a smooth surface, which is unfavorable to maximize the utilization of catalyst. Clearly, it can be seen from Fig.7(b) and Fig.7(c) that the novel catalyst layers based on surface-patterned Nafion[®] membranes have a three-dimensional curved surface structure, which can increase the surface roughness and the contact area between catalyst layer and electrolyte membrane. The curved surface structure optimizes the diffusion layer/catalyst layer interfacial structure, which is beneficial for reactants to expand considerably in the depth direction into the inner part of the catalyst layer, reducing the adverse effects of ridges on the catalyst layer. The increase of electrolyte/catalyst layer interfacial zone enlarges the “three-phase boundaries (TPB)” of MEA. Meanwhile, the surface of cathode catalyst layer is rougher than that of the anode, which is mainly attributed to the higher load of catalyst for anode.

This result can explain why the electrocatalytic performance of cathode increases more obviously. As shown in Fig.7(c), the catalyst layer surface of MEA-HP-2.5Mpa have some cracks, which is likely to be caused by the deep dents when the pressure is too high. The results indicate that performance degradation for the MEA-HP-2.5Mpa is caused by the cracks in catalyst layer.

Electrochemical surface area (ECSA) is widely used to characterize the anode and cathode electrocatalytic activity in DMFC. Therefore, the anode and cathode CV curves of each sample were in-situ measured and shown in Fig.8. Clearly, it can be seen that the ECSA initially increased significantly with increasing the pressure from 0.5Mpa to 1.5 Mpa and peaked for the sample MEA-HP-1.5Mpa before it decreased when further increasing the pressure to 2.5 Mpa. This result coincides with the performance change trend in peak power density of the MEAs. The anode and cathode ECSA values of MEA-HP-1.5Mpa is $29.03 \text{ m}^2 \text{ g}^{-1}$ and $38.7 \text{ m}^2 \text{ g}^{-1}$, increased by 43.4% and 79.3% respectively compared with MEA-HP-0Mpa. These datas indicate that the novel catalyst layer based on the surface-patterned Nafion[®] membrane can achieve more catalytic active sites and increase the “three-phase boundaries (TPB)”, which increases the reaction area and improves the catalyst utilization obviously.

4. Conclusions

The results obtained in this study showed that performance of DMFC can be improved by optimizing the electrolyte/catalyst layer and gas diffusion layer/catalyst layer interfacial structure based on surface-patterned Nafion[®] membrane. As-prepared surface-patterned Nafion[®] membranes under different pressures had different surface roughness and structures, which directly affected the surface structure of the catalyst layer. The pressure of hot pressing should be controlled to avoid the cracks in catalyst layer. Best performance was found for MEA-HP-1.5Mpa, and peak power density reached 252.72 mW cm⁻², which was increased by 28.84% than that of MEA-HP-0Mpa. EIS measurements indicated that the charge transfer resistances of anode and cathode reduced by 28.8% and 26.5% respectively. Surface and cross-section SEM images of the anode and cathode catalyst layer corresponding to different MEAs showed the novel catalyst layer with surface-pattered membrane has a three-dimensional curved surface structure, which can increase the surface roughness and contact area between catalyst layer and electrolyte membrane. The improvement of electrochemical surface area (ECSA) further proved the novel catalyst layer expands the electrochemical reaction zone and increases the “three-phase boundaries (TPB)”. Based on the above research results, the novel catalyst layer structure can be used to prepare high-performance MEA with lower Pt loading in the future.

Acknowledgements

This work was supported by NSFC-Liaoning Joint Funding (Grant No. U1508202), National Natural Science Foundation of China (Grant No.51774028), the 973 program of China (Project No.2013CB934002) and Key Research and Development Program of Beijing (Grant No.Z171100000917010).

Reference

- [1] S.K. Kamarudin, W.R.W. Daud, S.L. Ho, U.A. Hasran, Overview on the challenges and developments of micro-direct methanol fuel cells (DMFC), J. Power Sources 163 (2007) 743-754.
- [2] S.K. Kamarudin, F. Achmad, W.R.W. Daud, Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices, Int. J. Hydrog. Energy 34

(2009) 6902-6916.

[3] N. Kimiaie, K. Wedlich, M. Hehemann, R. Lambertz, M. Müller, C. Korte, D. Stolten, Results of a 20000 h lifetime test of a 7 kW direct methanol fuel cell (DMFC) hybrid system – degradation of the DMFC stack and the energy storage, *Energy Environ. Sci.* 7 (2014) 3013-3025.

[4] M. Wang, X. Wang, M. Chen, Z. Yang, C. Dong, Nanostructured electrocatalytic materials and porous electrodes for direct methanol fuel cells, *Chin. J. Catal.* 37 (2016) 1037-1048.

[5] S. Kim, S. Jang, S.M. Kim, C.-Y. Ahn, W. Hwang, Y.-H. Cho, Y.-E. Sung, M. Choi, Reduction of methanol crossover by thin cracked metal barriers at the interface between membrane and electrode in direct methanol fuel cells, *J. Power Sources* 363 (2017) 153-160.

[6] P. Kumar, P.P. Kundu, Coating and lamination of Nafion117 with partially sulfonated PVdF for low methanol crossover in DMFC applications, *Electrochim. Acta* 173 (2015) 124-130.

[7] S. Mondal, S. Malik, Easy synthesis approach of Pt-nanoparticles on polyaniline surface: an efficient electro-catalyst for methanol oxidation reaction, *J. Power Sources* 328 (2016) 271-279.

[8] G. Wu, L. Li, B.Q. Xu, Effect of electrochemical polarization of PtRu/C catalysts on methanol electrooxidation, *Electrochim. Acta* 50 (2004) 1-10.

[9] B. Ruiz-Camacho, J.H. Martínez-González, R.G. González-Huerta, M. Tufiño-Velázquez, Kinetic study of oxygen reduction reaction and PEM fuel cell performance of Pt/TiO₂-C electrocatalyst, *Int. J. Hydrog. Energy* 39 (2014) 16731-16739.

[10] S.M. Alia, K. Jensen, C. Contreras, F. Garzon, B. Pivovar, Y. Yan, Platinum Coated Copper Nanowires and Platinum Nanotubes as Oxygen Reduction Electrocatalysts, *Acs Catal.* 3 (2013) 358-362.

[11] P. Hartmann, D. Gerteisen, Local degradation analysis of a real long-term operated DMFC stack MEA, *J. Power Sources* 219 (2012) 147-154.

[12] A. Mehmood, M.-G. An, H.Y. Ha, Physical degradation of cathode catalyst layer:

- A major contributor to accelerated water flooding in long-term operation of DMFCs, *Appl. Energy* 129 (2014) 346-353.
- [13] S.K. Kamarudin, N. Hashim, Materials, morphologies and structures of MEAs in DMFCs, *Renew Sustain. Energy. Rev.* 16 (2012) 2494-2515.
- [14] Z. Long, G. Deng, C. Liu, J. Ge, W. Xing, S. Ma, Cathode catalytic dependency behavior on ionomer content in direct methanol fuel cells, *Chin. J. Catal.* 37 (2016) 988-993.
- [15] X. Zhao, W. Li, Y. Fu, A. Manthiram, Influence of ionomer content on the proton conduction and oxygen transport in the carbon-supported catalyst layers in DMFC, *Int. J. Hydrog. Energy* 37 (2012) 9845-9852.
- [16] K. Su, X. Yao, S. Sheng, Z. Wei, J. Zhang, S. Du, Ionomer content effects on the electrocatalyst layer with in-situ grown Pt nanowires in PEMFCs, *Int. J. Hydrog. Energy* 39 (2014) 3219-3225.
- [17] G. Liu, M. Wang, Y. Wang, Z. Tian, X. Wang, A novel anode catalyst layer with multilayer and pore structure for improving the performance of a direct methanol fuel cell, *Int. J. Energ. Res.* 37 (2012) 1313-1317.
- [18] G. Liu, X. Ding, H. Zhou, M. Chen, M. Wang, Z. Zhao, Z. Yin, X. Wang, Structure optimization of cathode microporous layer for direct methanol fuel cells, *Appl. Energy* 147 (2015) 396-401.
- [19] S. Kim, J.E. Park, W. Hwang, Y.-H. Cho, Y.-E. Sung, A hierarchical cathode catalyst layer architecture for improving the performance of direct methanol fuel cell, *Appl. Catal. B: Environ.* 209 (2017) 91-97.
- [20] T. Wang, C. Lin, F. Ye, Y. Fang, J. Li, X. Wang, MEA with double-layered catalyst cathode to mitigate methanol crossover in DMFC, *Electrochem. Commun.* 10 (2008) 1261-1263.
- [21] M. Prasanna, E.A. Cho, H.J. Kim, T.H. Lim, I.H. Oh, S.-A. Hong, Effects of platinum loading on performance of proton-exchange membrane fuel cells using surface-modified Nafion® membranes, *J. Power Sources* 160 (2006) 90-96.
- [22] A. Omosebi, R.S. Besser, Electron beam patterned Nafion membranes for DMFC applications, *J. Power Sources* 228 (2013) 151-158.

- [23] S.A. Cho, E.A. Cho, I.H. Oh, H.J. Kim, H.Y. Ha, S.A. Hong, J.B. Ju, Surface modified Nafion® membrane by ion beam bombardment for fuel cell applications, *J. Power Sources* 155 (2006) 286-290.
- [24] M.H. Yildirim, J. te Braake, H.C. Aran, D.F. Stamatialis, M. Wessling, Micro-patterned Nafion membranes for direct methanol fuel cell applications, *J. Membr. Sci.* 349 (2010) 231-236.
- [25] J.W. Bae, Y.-H. Cho, Y.-E. Sung, K. Shin, J.Y. Jho, Performance enhancement of polymer electrolyte membrane fuel cell by employing line-patterned Nafion membrane, *J. Ind. Eng. Chem.* 18 (2012) 876-879.
- [26] Y.-H. Cho, J. Woo Bae, O.-H. Kim, J. Young Jho, N. Jung, K. Shin, H. Choi, H. Choe, Y.-H. Cho, Y.-E. Sung, High performance direct methanol fuel cells with micro/nano-patterned polymer electrolyte membrane, *J. Membr.Sci.* 467 (2014) 36-40.
- [27] L. Pu, J. Jiang, T. Yuan, J. Chai, H. Zhang, Z. Zou, X.-M. Li, H. Yang, Performance improvement of passive direct methanol fuel cells with surface-patterned Nafion® membranes, *Appl. Surf. Sci.* 327 (2015) 205-212.
- [28] L. Sun, R. Ran, G. Wang, Z. Shao, Fabrication and performance test of a catalyst-coated membrane from direct spray deposition, *Solid State Ionics* 179 (2008) 960-965.
- [29] G. Liu, Z. Yang, M. Halim, X. Li, M. Wang, J.Y. Kim, Q. Mei, X. Wang, J.K. Lee, A gradient activation method for direct methanol fuel cells, *Energy Convers. Manage.* 138 (2017) 54-60.
- [30] G. Liu, X. Li, M. Wang, M. Wang, J.Y. Kim, J.Y. Woo, X. Wang, J.K. Lee, A study on anode diffusion layer for performance enhancement of a direct methanol fuel cell, *Energy Convers. Manage.* 126 (2016) 697-703.
- [31] Y. Wang, L. Zheng, G. Han, L. Lu, M. Wang, J. Li, X. Wang, A novel multi-porous and hydrophilic anode diffusion layer for DMFC, *Int. J. Hydrog. Energy* 39 (2014) 19132-19139.
- [32] G. Liu, X. Li, H. Wang, X. Liu, M. Chen, J.Y. Woo, J.Y. Kim, X. Wang, J.K. Lee, Design of 3-electrode system for in situ monitoring direct methanol fuel cells during

long-time running test at high temperature, Appl. Energy 197 (2017) 163-168.

[33] Y. Wang, G. Liu, M. Wang, G. Liu, J. Li, X. Wang, Study on stability of self-breathing DFMC with EIS method and three-electrode system, Int. J. Hydrog. Energy 38 (2013) 9000-9007.

[34] N.-Y. Hsu, S.-C. Yen, K.-T. Jeng, C.-C. Chien, Impedance studies and modeling of direct methanol fuel cell anode with interface and porous structure perspectives, J. Power Sources 161 (2006) 232-239.

[35] C.Y. Du, T.S. Zhao, C. Xu, Simultaneous oxygen-reduction and methanol-oxidation reactions at the cathode of a DMFC: A model-based electrochemical impedance spectroscopy study, J. Power Sources 167 (2007) 265-271.

[36] T.V. Reshetenko, H.-T. Kim, H.-J. Kweon, Modification of cathode structure by introduction of CNT for air-breathing DMFC, Electrochim. Acta 53 (2008) 3043-3049.

Captions for Figures in manuscript

Fig.1. Schematic diagram of enlarging electrochemical reaction interface for novel catalyst layer structure based on surface-patterned Nafion[®] membrane

Fig.2. Schematic diagram of fabrication for MEA with novel catalyst layer structure based on surface-patterned Nafion[®] membrane

Fig.3. SEM images of the surface and cross-section (illustration) morphology of surface-patterned Nafion[®] membranes under different pressure conditions:(a) 0Mpa; (b) 0.5Mpa; (c) 1.0Mpa; (d) 1.5Mpa; (e)2.0Mpa; (f) 2.5Mpa

Fig.4. Swelling degrees and Proton conductivities of surface-patterned Nafion[®] membranes under different pressure conditions

Fig.5. Polarization curves and power density curves of DMFCs with surface-patterned Nafion[®] membranes under different pressure conditions

Fig.6. (a) Anode and cathode polarization curves; (b) Methanol crossover measurements; (c) Electrochemical impedance spectroscopy measured at 400mA cm⁻²; (d) Results of equivalent circuit for the EIS analysis for DMFCs with surface-patterned Nafion[®] membranes under different pressure conditions.

Fig.7. SEM images of the surface and cross-section (illustration) morphology of membrane electrode assemblies:(a) MEA-HP-0Mpa; (b) MEA-HP-1.5Mpa; (c) MEA-HP-2.5Mpa

Fig.8. Cyclic voltammetry curves of anode (a) and cathode (b) for different MEAs

Captions for Tables in manuscript

Table 1 Fitted parameters for the equivalent circuit model for the different DMFCs operating at 400mA cm^{-2}

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400mA cm⁻²

Parameter	MEA-HP-0Mpa	MEA-HP-0.5Mpa	MEA-HP-1.5Mpa	MEA-HP-2.5Mpa
L_1 (H cm ⁻²)	8.11E-8	8.01E-8	8.04E-8	8.04E-8
R_m (Ω cm ²)	0.155	0.160	0.163	0.168
R_c (Ω cm ²)	0.243	0.219	0.173	0.278
Q_1 (F.cm ⁻²)	0.852	0.830	0.802	0.882
n_1	0.755	0.695	0.665	0.651
R_a (Ω cm ²)	0.215	0.200	0.158	0.235
Q_2 (F.cm ⁻²)	0.703	0.753	0.893	0.652
n_2	0.998	0.978	0.958	0.948
R_4 (Ω cm ²)	0.021	0.031	0.050	0.016
L_2 (H cm ⁻²)	0.022	0.018	0.013	0.026

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Highlights

- A novel catalyst layer based surface-patterned Nafion[®] membrane was designed and prepared.
- The novel catalyst layer optimizes the electrolyte membrane/catalyst layer and gas diffusion layer/catalyst layer interfacial structure.
- The peak power density of DMFC increased by 28.84% compared with the conventional catalyst layer.